# Enamines as 1,3-Dipolarophiles[1]

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The reactions of benzhydroxamoyl chloride and N¹-α-chlorobenzylidene-N²-phenylhydrazine with a number of cyclic and acyclic enamines led to aminodihydroisoxazoles and a pyrrolidinodihydropyrrazole. Elimination of the tertiary amine from the substituted heterocycles gave the corresponding isoxazoles and tetrahydroisoindazoles.

Extensions of the Stork acylation and alkylation reactions of enamines[3,4] have led to the direct formation of four-[5] and six-membered[6] carbocyclic ring systems, as well as γ-pyrones.[7] In each instance the products arise by generation and collapse of a dipolar immonium anion intermediate, formed from uncharged precursors (*i.e.*, Chart I). Even in the reaction of an enamine with benzyne,[8] where addition of a proton source can prevent cyclization to a benzocyclobutene, this two-step reaction path is evident.

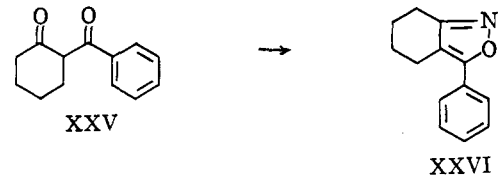
Direct formation of four-membered rings from reactions of enamines with ketenes,[9-11] with diethyl acetylenedicarboxylate,[12] and with alkyl sulfonyl chlorides[13,14] is also known.

The present study shows the direct formation of five-membered heterocyclic systems by reactions of enamines with two 1,3-dipolar species. While this work was in progress, syntheses of 1,2,3-triazoles were reported using other enamines and aryl and arylsulfonyl azides as alternative 1,3-dipolar reactants.[15-17]

As outlined by Huisgen,[18] the reaction of benzhydroxamoyl chloride (I) with base generates the 1,3-dipolar nitrile oxide II. When benzhydroxamoyl chloride (I) was added to 2 equiv. of the enamines III to X, the crystalline aminodihydroisoxazoles XII to XIX were formed in good yield. Alternatively, the reaction could be achieved with 1 equiv. of enamine and 1 equiv. of triethylamine as base. Only the morpholinodihydroisoxazole XX remained noncrystalline and had to be identified through the corresponding isoxazole XXII (see Chart II).

Pyrrolidine was readily eliminated on acid treatment of the aminodihydroisoxazoles XIII and XIV, derived from the six- and seven-membered carbocyclic enamines. However, the next lower homolog XII was stable in refluxing hydrochloric acid, and removal of the pyrrolidine ring could only be achieved by Hofmann degradation. The greater ease of elimination of pyrrolidine from the higher homologs XIII and XIV reflects greater flexibility of the four- and five-carbon bridges on the isoxazoles XXII and XXIII as compared with the more rigid three-carbon bridge in XXI, which imposes some steric strain on the isoxazole system. The decreasing strain on the heterocycle in the homologous series XXI, XXII, and XXIII is also reflected by the corresponding ultraviolet absorption maxima at 240, 236, and 229 mμ.

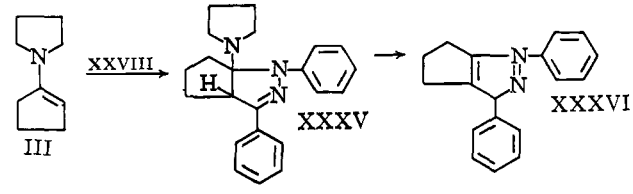
Preparation of the isoxazole XXII, derived from 1-pyrrolidinocyclohexene (IV) by the present route, now also allows structural assignment to the isoxazole obtained from 2-benzoylcyclohexanone XXV and hydroxylamine,[19] where the isomeric product XXVI with ultraviolet absorption at 266 mμ is obtained.



XXV XXVI

Addition of N¹-α-chlorobenzylidene-N²-phenylhydrazine (XXVII) to 1-pyrrolidinocyclohexene (IV), with triethylamine or excess enamine acting as base for liberation of the 1,3-dipolar diphenylnitrilimine XXVIII,[20] led directly to the diphenyltetrahydroisoindazole XXIX. Similarly, the enamines derived from piperidine and hexamethyleneimine and cyclohexanone VI and XXX gave the same product, and the pyrrolidine enamines of 4-benzoyloxycyclohexanone XXXI, cycloheptanone V, and benzyl phenyl ketone X gave the pyrazoles XXXII–XXXIV (see Scheme I).

Only from the reaction of 1-pyrrolidinocyclopentene III could the intermediate pyrrolidinodihydropyrazole XXXV be isolated. On mild acid treatment of this product, the trimethylenepyrazole XXXVI was formed. Again, as with the isoxazoles, the homologous series of pyrazoles fused to five-, six- and seven-membered carbocyclic rings shows decreasing ultraviolet absorption maxima in 287, 276, and 268 mμ.



III XXXV XXXVI

(1) Taken in part from M.S. thesis in chemistry of S. J. Weaver, submitted May, 1963.

(2) Undergraduate research participant, Spring 1963.

(3) G. Stork, R. Terrell, and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **76**, 2029 (1954).

(4) G. Stork and H. K. Landesman, *ibid.*, **78**, 5128, 5129 (1956).

(5) K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelley, *J. Org. Chem.*, **26**, 625 (1961).

(6) G. Stork, A. Brizzolara, H. Landesman, J. Smuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

(7) S. Hünig, E. Benzing, and K. Hübner, *Ber.*, **94**, 486 (1961).

(8) M. E. Kuehne, *J. Am. Chem. Soc.*, **84**, 837 (1962).

(9) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **26**, 4775 (1961); **28**, 1468 (1963).

(10) G. Opitz, H. Adolph, M. Kleemann, and F. Zimmermann, *Angew. Chem.*, **73**, 654 (1961).

(11) G. Opitz, M. Kleemann, and F. Zimmermann, *ibid.*, **74**, 32 (1962).

(12) K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, *J. Org. Chem.*, **28**, 1464 (1963).

(13) G. Stork and I. Borowtiz, *J. Am. Chem. Soc.*, **84**, 313 (1962).

(14) G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962).

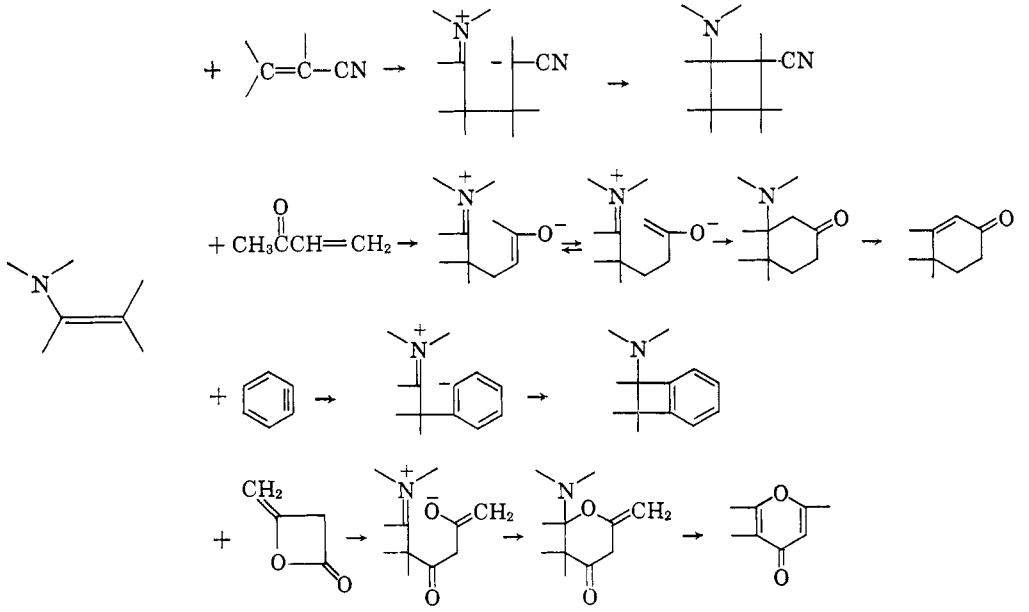
(15) (a) G. Nathanson, E. Testa, and N. Di Mola, *Experientia*, **18**, 57 (1962); (b) Morton E. Munk and Yung K. Kim, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 29Q.

(16) R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Ber.*, **96**, 802 (1963).

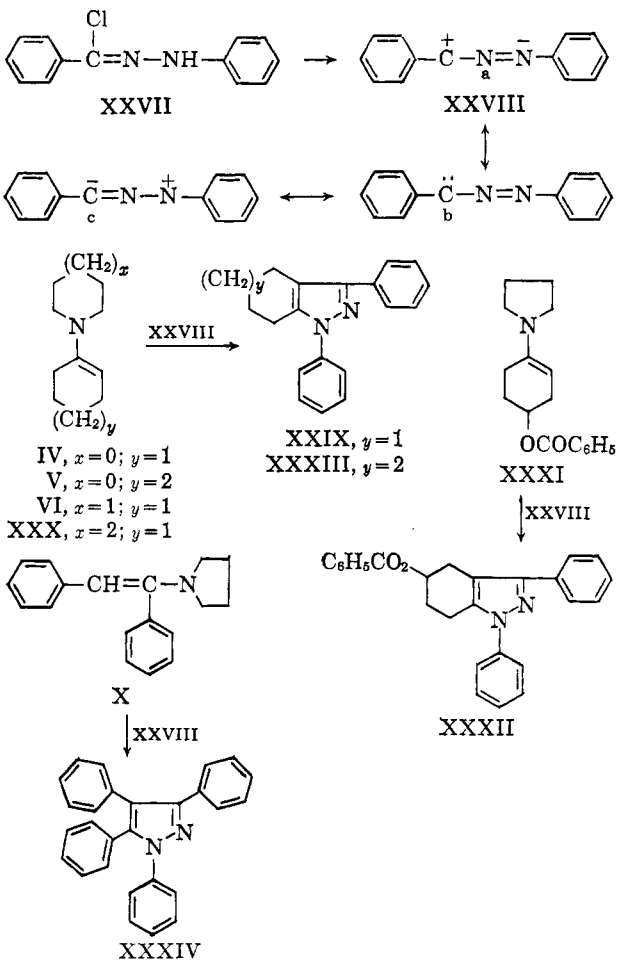
(17) R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Gazz. chim. ital.*, **91**, 849, 933 (1961); **92**, 1040 (1962).

(18) R. Huisgen, *Proc. Chem. Soc.*, 357 (1961).

CHART I

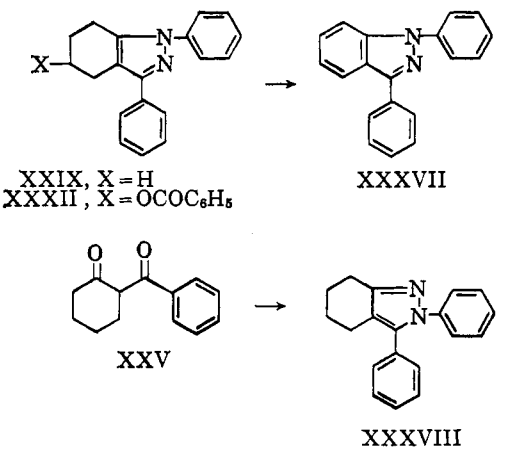


SCHEME I




Addition of the diphenylnitrilimine XXVIII to 1-pyrrolidinocyclohexene (IV) was also examined in a number of polar and nonpolar solvents under standard conditions. No significant changes in yields were apparent, suggesting a four-center mechanism rather than a polarized intermediate for this reaction.

Dehydrogenation of the tetrahydroisoindazoles XXIX, m.p. 131°, and XXXII to the known 1,3-diphenylisoindazole XXXVII and comparison of the tetraphenylpyrazole XXXIV with an authentic sample established the structures of these compounds. The present sequence also establishes the structure XXXVIII of the isomeric pyrazole, m.p. 11°, from 2-benzoylcyclohexanone XXV and phenylhydrazine.[19]

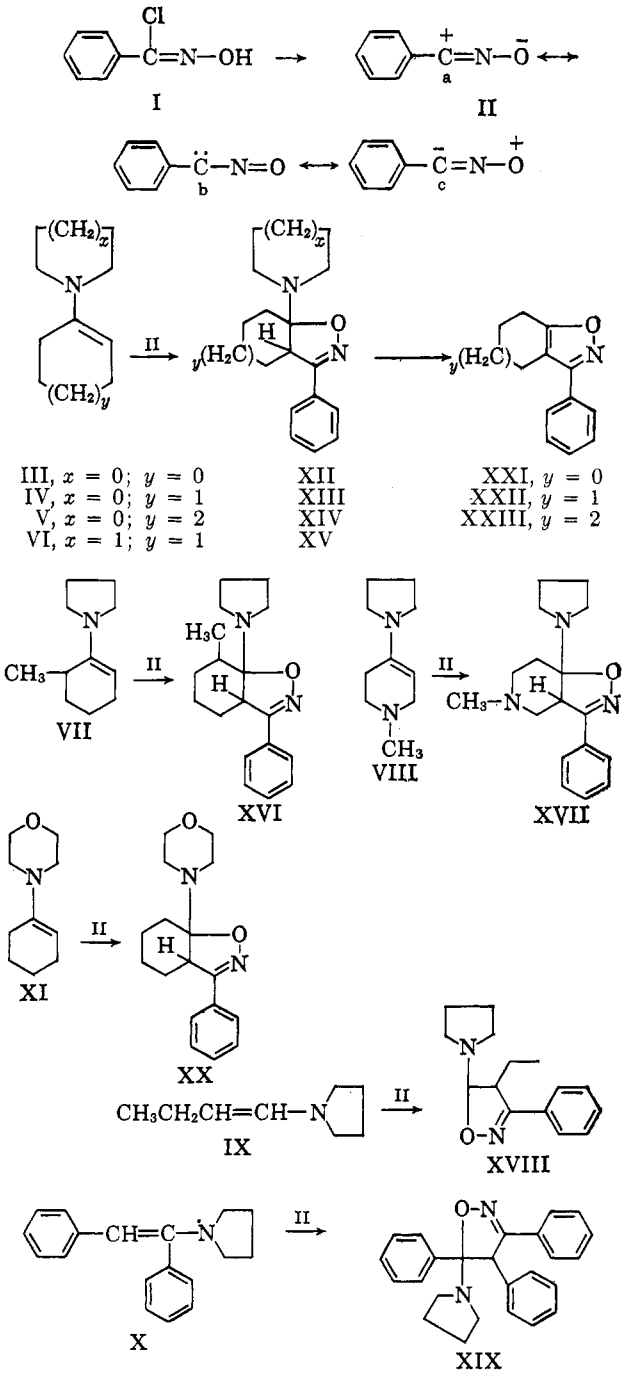



Although one might expect addition of the two dipolar species to enamines to proceed through a polarized stage with electron deficiency on carbon (IIa and XXVIIIa) rather than on oxygen or nitrogen (IIc and XXVIIIc), it was necessary to establish this mode of addition since it has been found that both additions to polarized double bonds are possible.[20] Structural assignments of the pyrrolidinodihydroisoxazoles and the pyrrolidinotrimethylenedihydropyrazole XXXV could be derived from n.m.r. spectra. The latter compound as well as the corresponding dihydroisoxazole XII showed the expected multiplets for the angular proton to have identical chemical shifts centered at $\tau$ 6.28. A difference in chemical shifts would be expected for the aminodihydroisoxazole and the aminodihydropyrazole if the alternative structures to XII

(19) E. Bauer, *Ann. chim.*, **1**, 393 (1914).

(20) R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*; **17**, 3 (1962).

CHART II




and XXXV were present, with the angular hydrogen then on a carbon atom substituted by oxygen or nitrogen, respectively. Comparison of the trimethylene-dihydroisoxazole XII with the tetramethylene compound XIII shows less deshielding of the angular proton, now centered at $\tau$ 6.57, in the higher homolog.

The chemical shifts of the angular protons compare favorably with the $\tau$ 6.38 value for the tertiary hydrogen multiplet of the isobutyrophenone oxime isomer, where phenyl and hydroxyl groups have the *anti* orientation.[21] The other isobutyrophenone oxime isomer,[21] with hydroxyl and phenyl groups *syn*, gave a tertiary hydrogen multiplet at $\tau$ 7.15. This difference in chemical shifts of the $\alpha$-hydrogens between *syn* and *anti* isomers of the oxime, in accord with a recent report on a number of isomeric pairs[22] of oximes and hydrazones, was also found in the isobutyrophenone phenylhydrazone pair with chemical shifts of the tertiary hydrogen multiplet centered at $\tau$ 6.95 and 7.23. The fixed spacial orientation and identical chemical shift of the angular hydrogen in the dihydroisoxazole XII and the dihydropyrazole XXXV is not found in the analogous, but less rigid, butyrophenone oxime and phenylhydrazone.

(21) H. M. Kissman and J. Williams, *J. Am. Chem. Soc.*, **72**, 5223 (1950).

## Experimental

The enamines used in the following experiments were prepared according to previous procedures.[8,23] The enamine 1-pyrrolidinobutene IX, b.p. 87–90° (65 mm.), 48% yield, was prepared according to the procedure of Opitz.[24]

*Anal.* Calcd. for $C_8H_{15}N$: C, 76.84; H, 12.08; N, 11.19. Found: C, 76.60; H, 12.01; N, 11.37.

The new enamine, 1,2-diphenyl-1-pyrrolidinoethylene (X), m.p. 42–43°, was prepared by Mr. Charles Bayha of this research group by azeotropic distillation of water from a benzene solution of equimolar amounts of desoxybenzoin and pyrrolidine, and crystallization from petroleum ether (b.p. 30–60°).

*Anal.* Calcd. for $C_{18}H_{19}N$: C, 86.68; H, 7.68; N, 5.62. Found: C, 86.90; H, 7.70; N, 5.92.

**4,5-Dihydro-4-pyrrolidino-3-phenyl-4,5-tetramethyleneisoxazole (XIII).**—A solution of 0.60 g. (3.8 mmoles) of benzhydroxamoyl chloride[25] and 1.8 g. (12.0 mmoles) of 1-pyrrolidinocyclohexene in 30 ml. of dichloromethane was stirred at room temperature for 15 hr., the solvent evaporated, and about 20 ml. of water was added to the residue. Filtration and recrystallization from aqueous ethanol gave 1.0 g. (97% yield) of product, m.p. 103–104°. All other aminodihydroisoxazoles were prepared under the same conditions (see Table I).

**3-Phenyl-4,5-tetra- and -pentamethyleneisoxazoles (XXII and XXIII.)**—Solutions of 0.50 g. of the aminodihydroisoxazoles XIII and XIV in 5 ml. of methanol and 8 ml. of concentrated hydrochloric acid were boiled for 20 min., cooled, and neutralized with aqueous sodium bicarbonate. Filtration and recrystallization from aqueous ethanol gave 0.33 g. (91% yield) of XXII, m.p. 53–54°, ultraviolet absorption $\lambda_{max}^{cyclohexane}$ 236 m$\mu$ (log $\epsilon$ 4.18), and 0.35 g. (91% yield) of XXIII, m.p. 83–84°, ultraviolet absorption $\lambda_{max}^{cyclohexane}$ 229 m$\mu$ (log $\epsilon$ 4.09).

*Anal.* Calcd. for $C_{13}H_{13}NO$: C, 78.32; H, 6.57; N, 7.03. Found: C, 77.92; H, 6.84; N, 6.36.

*Anal.* Calcd. for $C_{14}H_{15}NO$: C, 78.86; H, 7.09; N, 6.57. Found: C, 78.65; H, 7.10; N, 6.76.

The crude oily morpholinodihydroisoxazole XX, from 1.0 g. of benzhydroxamoyl chloride and 2.7 g. of enamine XI gave 0.35 g. (28% over-all yield) of isoxazole XXII.

In comparison, a sample of the isoxazole XXVI,[19] prepared by refluxing equimolar quantities of 2-benzoylcyclohexanone, hydroxylamine hydrochloride, and excess sodium carbonate in aqueous ethanol showed m.p. 66–67°, ultraviolet absorption $\lambda_{max}^{cyclohexane}$ 226 m$\mu$ (log $\epsilon$ 4.32).

*Anal.* Calcd. for $C_{13}H_{13}NO$: C, 78.32; H, 6.57; N, 7.03. Found: C, 78.60; H, 6.50; N, 7.12.

**3-Phenyl-4,5-trimethyleneisoxazole (XXI).**—A solution of 0.10 g. of the aminodihydroisoxazole XII in 5 ml. of methyl iodide was evaporated to dryness after 3 days at room temperature. After grinding with 0.30 g. of silver oxide, the mixture was heated to 220° at 0.05 mm. and the sublimed product was recrystallized from aqueous ethanol, m.p. 79–80°, ultraviolet absorption $\lambda_{max}^{cyclohexane}$ 240 m$\mu$ (log $\epsilon$ 4.07).

*Anal.* Calcd. for $C_{12}H_{11}NO$: C, 77.82; H, 5.98; N, 7.56. Found: C, 77.83; H, 5.86; N, 7.58.

**Reactions of Enamines with Diphenylnitrilimine XXVIII. 1,3-Diphenyl-4,5,6,7-tetrahydroisoindazole (XXIX).**—To 0.61 g. (0.0027 mole) of N$^1$-$\alpha$-chlorobenzylidene-N$^2$-phenylhydrazine (XXVII)[26] in 20 ml. of dichloromethane, under nitrogen, was added 1.1 ml. (0.0081 mole) of 1-pyrrolidinocyclohexene (IV).

(22) G. J. Karabatsos, R. A. Taller, and F. M. Vane, *ibid.*, **85**, 2326, 2327 (1963).

(23) M. E. Kuehne, *ibid.*, **81**, 5400 (1959).

(24) G. Opitz and H. Mildenberger, *Ann.*, **649**, 26 (1961).

(25) A. Werner and H. Buss, *Ber.*, **27**, 2193 (1894).

(26) H. V. Pechman, *ibid.*, **27**, 320 (1894).

TABLE I

AMINODIHYDROISOXAZOLES

| Compound | Empirical formula | M.p., °C. | Yield, % | Calcd., % / Found, % —C— | —H— | —N— |
|---|---|---|---|---|---|---|
| XII | $C_{16}H_{20}N_2O$ | 83–84 | 56 | 74.94 | 7.86 | 10.92 |
| | | | | 74.64 | 7.71 | 10.82 |
| XIII | $C_{17}H_{22}N_2O$ | 103–104 | 97 | 75.51 | 8.20 | 10.36 |
| | | | | 75.23 | 8.00 | 10.23 |
| XIV | $C_{18}H_{24}N_2O$ | 114–115 | 74 | 76.01 | 8.51 | 9.85 |
| | | | | 75.65 | 8.78 | 9.59 |
| XV | $C_{18}H_{24}N_2O$ | 132–133 | 64 | 76.01 | 8.51 | 9.85 |
| | | | | 75.72 | 8.37 | 9.92 |
| XVI | $C_{18}H_{24}N_2O$ | 163–164 | 64 | 76.01 | 8.51 | 9.85 |
| | | | | 75.68 | 8.59 | 9.59 |
| XVII | $C_{17}H_{23}N_3O$ | 118–119 | 82 | 71.54 | 8.12 | 14.73 |
| | | | | 71.75 | 8.18 | 14.48 |
| XVIII | $C_{16}H_{22}N_2O$ | 60–62 | 35 | 74.36 | 8.58 | 10.83 |
| | | | | 74.12 | 8.40 | 10.70 |
| XIX | $C_{25}H_{24}N_2O$ | 210–212 | 75 | 81.48 | 6.57 | 7.60 |
| | | | | 81.34 | 6.60 | 7.44 |

TABLE II

FORMATION OF AMINODIHYDROPYRAZOLES

| Reactant | Product | Empirical formula | M.p., °C. | Yield, % | Ultraviolet spectra,[a] λ, mμ (log ε) | Calcd., % / Found, % —C— | —H— | —N— |
|---|---|---|---|---|---|---|---|---|
| IV | XXIX | $C_{19}H_{18}N_2$ | 130–131 | 77 | 276 (4.36) | 83.18 | 6.61 | 10.21 |
| | | | | | | 83.07 | 6.71 | 10.50 |
| VI | XXIX | $C_{19}H_{18}N_2$ | 130–131 | 13 | 276 (4.36) | | ... | |
| XXX | XXIX | $C_{19}H_{18}N_2$ | 130–131 | 58 | 276 (4.36) | | ... | |
| V | XXXIII | $C_{20}H_{20}N_2$ | 103–104 | 32 | 268 (4.22) | 83.29 | 6.99 | 9.71 |
| | | | | | | 82.97 | 7.00 | 9.71 |
| XXXI | XXXII | $C_{26}H_{21}N_2O_2$ | 161–162 | 74 | 277 (4.50) | 79.38 | 5.38 | 7.12 |
| | | | | | | 79.18 | 5.74 | 7.11 |
| X | XXXIV | $C_{27}H_{20}N_2$ | 217–218 | 21 | 238 (4.42) sh | | *b* | |
| | | | | | 273 (4.26) sh | | | |

[a] In cyclohexane. [b] Identical mixture melting point and infrared spectra with authentic sample.

After 18 hr. at room temperature the solvent was evaporated under vacuum, the residue was washed with water and triturated with methanol, and the 0.56 g. (77% yield) of crystalline product was filtered, m.p. 130–131° after recrystallization from ethanol. Other enamines reacted with diphenylnitrilimine under the same conditions to give the compounds listed in Table II. Reactions of 1-pyrrolidinocyclohexene with diphenylnitrilimine, generated in different solvents, are listed in Table III. In these reactions equivalent amounts of enamine IV, chlorobenzylidene compound XXVII, and triethylamine were used.

TABLE III

FORMATION OF 1,3-DIPHENYL-4,5,6,7-TETRAHYDROISOINDAZOLE

| Solvent system | Yield, % |
|---|---|
| Cyclohexane, room temp. | 37 |
| Dioxane, room temp. | 27 |
| Dimethylformamide, room temp. | 37 |
| Methylene chloride, room temp. | 39 |
| Benzene, reflux | 4 |
| Tetrahydrofuran, reflux | 0 |

**4,5-Dihydro-1,3-Diphenyl-5-pyrrolidyl-4,5-trimethylenepyrazole (XXXV) and 1,3-Diphenyl-4,5-trimethylenepyrazole (XXXVI).**—Under the standard conditions above (Table II) 0.80 g. (0.0035 mole) of N¹-α-chlorobenzylidene-N²-phenylhydrazine and 1.50 ml. (0.010 mole) of 1-pyrrolidinocyclopentene gave 0.92 g. (80% yield) of the aminodihydropyrazole XXXV, m.p. 99–100°, ultraviolet absorption $\lambda_{max}^{cyclohexane}$ 251 mμ (log ε 4.45), 299 (4.02). With equivalent amounts of enamine, chloro compound, and triethylamine, a 71% yield was obtained.

*Anal.* Calcd. for $C_{22}H_{25}N_3$: C, 79.71; H, 7.60; N, 12.68. Found: C, 79.42; H, 7.71; N, 12.76.

Refluxing a solution of 0.050 g. (0.00015 mole) of the aminodihydropyrazole XXXV in 5 ml. of ethanol and 10 ml. of 10% hydrochloric acid for 1 hr., cooling, and filtration gave 0.025 g. (64% yield) of the pyrazole XXXVI, m.p. 167–168° after recrystallization from ethanol, ultraviolet absorption $\lambda_{max}^{cyclohexane}$ 287 mμ (log ε 4.32).

*Anal.* Calcd. for $C_{18}H_{16}N_2$: C, 83.05; H, 6.19; N, 10.76. Found: C, 82.80; H, 6.03; N, 10.48.

**1,3-Diphenylisoindazole (XXXVII).**—A mixture 50 mg. (0.18 mmole) of 1,3-diphenyl-4,5,6,7-tetrahydroisoindazole and 100 mg. of 10% palladium on charcoal was heated at 260–265° for 2 hr. Addition of dichloromethane to the cooled material, filtration, evaporation, and recrystallization from ethanol gave 35 mg. (71% yield), m.p. 101–102°, lit.[27] m.p. 100–101°.

**Isobutyrophenone Phenylhydrazones.**—A combination of equivalent amounts of phenylhydrazine and isobutyrophenone was treated after 24 hr. at 20° with petroleum ether. The mixture of phenylhydrazones, obtained in almost quantitative yield, was filtered and recrystallized from ligroin to m.p. 55–57°, lit.[28] m.p. 73°. The material was quite unstable. When left at room temperature, exposed to air, it quickly turned brown and after some hours to a black oil. A fresh solution in deuteriochloroform showed n.m.r. multiplets centered at τ 6.95 and 7.23 corresponding to the tertiary hydrogen of the isomeric phenylhydrazones. The methyl doublets of the isomeric phenylhydrazones were found at τ 8.78 and 8.86, respectively. After 24 hr. a solution of the phenylhydrazone mixture in carbon tetrachloride showed only the chemical shifts of one phenylhydrazone isomer at τ 6.95 and 8.78. All n.m.r. spectra were obtained with a Varian A-60 instrument.

(27) W. Borsch and W. Scriba, *Ann.*, **540**, 83 (1939).
(28) A. Klages, *Ber.*, **36**, 3688 (1903).

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# Photoisomerizations of 3,3′-Dinitro-4,4′-di(2-pyridylmethyl)azoxybenzene

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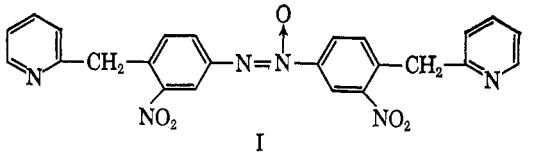
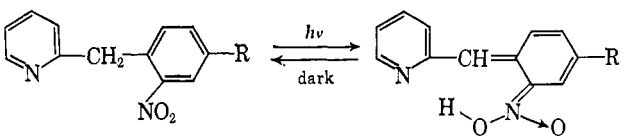
It is reported that, on irradiation with ultraviolet light, 3,3′-dinitro-4,4′-di(2-pyridylmethyl)azoxybenzene (I) undergoes simultaneously *aci*-nitro–nitro tautomerization and geometrical isomerization. Kinetic data at several temperatures are reported for the dark reverse reactions. The thermodynamic properties of the dark reactions are also given.

In a previous paper,[1] the preparation of 3,3′-dinitro-4,4′-di(2-pyridylmethyl)azoxybenzene (I) was reported. It was observed that, when cooled crystals are exposed to ultraviolet light, a photochromic change



I

from yellow to blue-green occurs. In room light the crystals fade to their original color. A reversible photochromism of cooled ethanol solutions of the compound was also noted. This behavior is similar to that observed for other *o*-nitrobenzylpyridines[1,2-6] and related compounds.[4,6-8] It is believed that the color change is due to the formation of the *aci*-nitro tautomer.[3-5,7]



In addition to the above structural change, I, on ultraviolet irradiation, might also undergo geometrical isomerization around the –N=N– bond. It was considered of interest to determine whether both photoisomerizations could be detected and isolated by spectrophotometric techniques, and, if so, to determine the kinetic and thermodynamic properties of the dark reactions.

## Results and Discussion

**Spectroscopic Studies.**—The ultraviolet and visible spectra of an ethanol solution of I before and after exposure to ultraviolet light are shown in Fig. 1. The absorption band at 610 mμ, observed on irradiation of the cooled solution, is similar in shape to the visible band reported[3,4] for the photoisomer of 2-(2,4-dinitrobenzyl)pyridine. This band decays rapidly when the exciting radiation is removed.

In the ultraviolet spectrum of the unirradiated sample, absorption bands are observed at 330 and 260 mμ. The effect of ultraviolet light on these bands can be observed at room temperature. The band at 330 mμ decreases markedly in intensity, while the absorbance at 260 mμ increases slightly. After irradiation the spectrum slowly reverts to that originally observed. The ultraviolet spectra before and after exposure closely resemble those reported[9] for the pure *trans* and *cis* isomers, respectively, of azoxybenzene and several of its derivatives. This geometrical photoisomerization also occurs at low temperatures.

The ultraviolet spectra of unirradiated ethanol and cyclohexane solutions of I were not temperature dependent. In these solutions the compound exists essentially in the *trans* configuration. Evidence for an equilibrium mixture of *cis* and *trans* forms was observed in the spectrum of an unirradiated ethanol solution of azoxybenzene. Exposure to ultraviolet light enriched the solution with respect to the *cis* isomer. The original equilibrium was restored when irradiation was discontinued.

**Kinetics.**—First-order kinetics was observed for the fading reaction of the photoisomer of I absorbing at 610 mμ. Although many aromatic azoxy compounds undergo a molecular rearrangement to *o*-hydroxyazo compounds on prolonged irradiation with ultraviolet light,[10,11] and 2-(2,4-dinitrobenzyl)pyridine decomposes on extended exposure,[3,4] no detectable irreversible change occurred during the short exposure times utilized in the rate measurements reported in this study. For example, the same value for the first-order rate constant was obtained after each of several exposures of an ethanol solution to radiation in the flash photolysis experiments at room temperature.

The correlation of log $k$ values with $1/T$, shown in Fig. 2, appears to be linear over a temperature range of 132°. The values of the Arrhenius activation energy, entropy of activation, and frequency factor were found to be 5.9 ± 0.1 kcal./mole, −39 e.u., and $4.2 \times 10^4$ sec.$^{-1}$, respectively. These values are consistent with those previously found for the thermal fading reaction

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