

$$2V_{b(ip)} = k_{bip}(\delta) \frac{R_1}{R_2} \left(1 + \frac{R_1}{R_2}\right) [(\Delta\epsilon)^2 + (\Delta\epsilon')^2]$$

From Fig. 2a

$$\Delta\epsilon \left(1 - \frac{R_1^2}{R_2^2}\right) = \theta_2 \left(1 - \frac{R_0}{R_2} \sin \beta\right) - \theta_1 \frac{R_H}{R_2} \sin \lambda$$

with a similar expression for  $\Delta\epsilon'$ , except that  $\theta_1, \theta_2$  are transposed. When these are squared, combined, and the potential function differentiated, the following components appear in the potential energy matrix

$$V_{X_1, X_1} = V_{X_2, X_2} = V_{X_1, X_2} = V_{X_2, X_1} = 2k_{st}$$

$$V_{\theta_1, \theta_1} = V_{\theta_1, \theta_2} = A \left[ \left(1 - \frac{R_0}{R_2} \sin \beta\right)^2 + \frac{R_H^2}{R_2^2} \sin^2 \lambda \right] + 2k_{bip}(\delta) R_0^2 \cos^2 \beta$$

$$V_{\theta_1, \theta_2} = V_{\theta_2, \theta_1} = -2A \left[ \left(1 - \frac{R_0}{R_2} \sin \beta\right) \frac{R_H}{R_2} \sin \lambda \right] + 2k_{bip}(\delta) R_0^2 \cos^2 \beta$$

where we have set

$$k_{bip}(\delta) \frac{R_1}{R_2} \left[1 + \frac{R_1}{R_2}\right] \left[1 - \frac{R_1^2}{R_2^2}\right]^{-2} = A$$

The secular determinant is therefore

$$\begin{vmatrix} 2k_{st} - M\omega^2 & 2k_{st} & 0 & 0 \\ 2k_{st} & 2k_{st} - M\omega^2 & 0 & 0 \\ 0 & 0 & V_{\theta_1, \theta_1} - I_x\omega^2 & V_{\theta_1, \theta_2} \\ 0 & 0 & V_{\theta_2, \theta_1} & V_{\theta_2, \theta_2} - I_x\omega^2 \end{vmatrix}$$

for which the roots are

$$\omega = 0 \quad \omega_1 = 2\sqrt{k_{st}/M}$$

$$\omega_2 = \sqrt{(V_{\theta_1, \theta_1} + V_{\theta_2, \theta_2})/I_x} \quad \omega_3 = \sqrt{(V_{\theta_1, \theta_1} - V_{\theta_2, \theta_2})/I_x}$$

These correspond to the frequencies listed in Table VI.

**The Out-of-plane Vibrations.**—The distances  $d_H$  and  $d_H'$  of Fig. 2a appear again in Fig. 2b, being the distances (in the inclined planes) from the axes  $y(1)$  and  $y(2)$  to the points 1 and 2, respectively. The latter are determined by the intersection of the inclined planes with the normal to the

original plane, which passes through the hydrogen atom. As before

$$k_{bop}(\alpha)/k_{bop}(\psi) \doteq R_2/R_1 \text{ and } \alpha/\omega \doteq R_1/R_2$$

$$2V_{b(op)} = k_{bop}(\alpha) \left[\alpha^2 + \frac{R_1}{R_2} \psi^2\right] + \text{similar terms in } \alpha', \psi'$$

The distance

$$\begin{aligned} \bar{12} &= d_H\theta_5 - d_H'\theta_7 + G(\theta_6 - \theta_8) \\ &= R_1\alpha + R_2\psi \end{aligned}$$

Hence

$$\psi = \frac{\bar{12} \cdot R_2}{R_1^2 + R_2^2}$$

Let

$$k_{bop}(\alpha) \frac{R_2^2}{(R_1^2 + R_2^2)^2} \left(1 + \frac{R_1}{R_2}\right) \frac{R_1}{R_2} = B$$

Then, the components of the potential energy matrix are

$$\begin{aligned} V_{55} &= V_{66} = B(d_H^2 + d_H'^2) \\ V_{56} &= V_{65} = -2Bd_Hd_H' \\ V_{57} &= V_{75} = V_{68} = V_{86} = -V_{58} = -V_{65} = -V_{67} = -V_{76} \\ &= BG(d_H - d_H') \\ V_{77} &= V_{88} = -V_{78} = -V_{87} = 2BG^2 \end{aligned}$$

The secular determinant takes the form

$$\begin{vmatrix} V_{55} - I_y\omega^2 & V_{56} & V_{57} & -V_{57} \\ V_{56} & V_{55} - I_y\omega^2 & -V_{57} & V_{57} \\ V_{57} & -V_{57} & V_{77} - I_x\omega^2 & -V_{77} \\ -V_{57} & V_{57} & -V_{77} & V_{77} - I_x\omega^2 \end{vmatrix}$$

the roots of which may be expressed as

$$\omega = 0 \quad \omega_4 = \sqrt{(V_{55} + V_{56})/I_y}$$

and

$$\begin{vmatrix} (V_{55} - V_{56}) - I_y\omega^2 & 2V_{57} \\ 2V_{57} & 2V_{77} - I_x\omega^2 \end{vmatrix} = 0$$

ITHACA, N. Y.

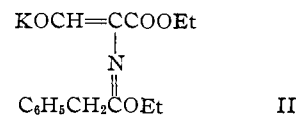
## NOTES

### Ethyl $\alpha$ -( $\alpha'$ -Ethoxy- $\beta'$ -phenylethylideneamino)- $\beta, \beta$ -diethoxypropionate

By HOMER ADKINS<sup>1</sup> AND GERALD GILBERT<sup>2</sup>

RECEIVED JULY 31, 1953

The projected synthesis of a series of substituted oxazolines required ethyl  $\alpha$ -( $\alpha'$ -ethoxy- $\beta'$ -phenylethylideneamino)- $\beta, \beta$ -diethoxypropionate (I) or the corresponding aldehyde as an intermediate. However, other investigations indicate that the presence of the free aldehyde is attended by cyclization. Thus, the condensation of ethyl phenyliminoacetate with the sodium enolate of ethyl N-formyl- $\alpha$ -formylglycinate in the presence of hydrogen chloride has been shown to yield 2-benzyl-4-carbethoxyoxazole.<sup>3</sup> The substituted iminoester, II



which is stabilized by the potassium enolate, was prepared by Tiffany<sup>4</sup> by another route. However, several attempts to produce I from this substance in the presence of some acetal-forming reagents again yielded 2-benzyl-4-carbethoxyoxazole.

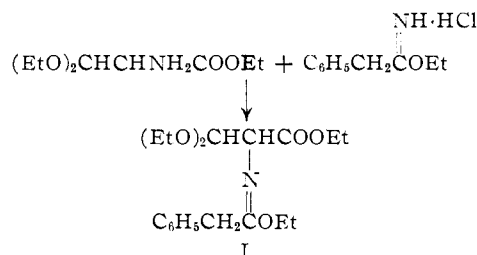
The present investigation indicates that cyclization can be avoided by preparing the acetal prior to the iminoester condensation. The reaction of ethyl  $\beta, \beta$ -diethoxyalanate with ethyl phenyliminoacetate hydrochloride proceeded readily in ethylene dichloride at room temperature and I was isolated in 70% yield.

(1) Deceased August 10, 1949.

(2) Rohm and Haas Co., Phila., Pa.

(3) H. Adkins, R. M. Ross and D. C. Schroeder, *THIS JOURNAL*, **72**, 5401 (1950).

(4) B. D. Tiffany, Ph.D. Thesis, University of Wisconsin, 1949; cf. J. W. Cornforth, E. Fawaz, L. J. Goldsworthy and R. Robinson, *J. Chem. Soc.*, 1549 (1949).



In some runs, phenylacetamide, which can arise from the decomposition of ethyl phenyliminoacetate hydrochloride,<sup>5</sup> was also found in the distillate.

#### Experimental

**Ethyl  $\alpha$ -( $\alpha'$ -Ethoxy- $\beta'$ -phenylethylideneamino)- $\beta,\beta$ -diethoxypropionate (I).**—In a 500-ml. flask fitted with a Hershberg stirrer were placed 25 g. (0.122 mole) of ethyl  $\beta,\beta$ -diethoxyalanate<sup>6</sup> and 37 g. (0.175 mole) of ethyl phenyliminoacetate hydrochloride<sup>7</sup> in 200 ml. of ethylene dichloride. The mixture usually became warm at the start and was cooled in an ice-bath. The bath was then removed and stirring continued at room temperature for 24 hours. The ammonium chloride was filtered from the product, the solvent removed under reduced pressure, and the residue fractionated through a 12-cm. Vigreux column; b.p. 125–127° (0.04 mm.), yield 30 g. (70%). The product was a light yellow oil, soluble in ether and insoluble in 10% hydrochloric acid.

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{29}\text{O}_5\text{N}$ : N, 3.99;  $\text{C}_2\text{H}_5\text{O}$ , 51.28. Found: N (Kjeldahl), 4.01, 3.96, 3.95;  $\text{C}_2\text{H}_5\text{O}$  (Zeisel), 51.12, 50.80.

In some runs, small amounts of a white crystalline solid, m.p. 160–161°, codistilled with the product. A mixed melting point with an authentic sample of phenylacetamide showed no depression.

*Anal.* Calcd. for  $\text{C}_9\text{H}_9\text{NO}$ : C, 71.09; H, 6.71; N, 10.36. Found: C, 70.80; H, 6.69; N, 10.41.

(5) S. M. McElvain and B. E. Tate, *THIS JOURNAL*, **73**, 2233 (1951).

(6) "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949, p. 512.

(7) S. M. McElvain and C. L. Stevens, *THIS JOURNAL*, **68**, 1917 (1946).

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### Spectroscopic Evidence for the Structure of Isoxazolines and the Mechanism of their Formation<sup>1,2</sup>

BY R. PERCY BARNES, GLADYS ESTELLE PINKNEY<sup>3</sup> AND  
GEORGE MCK. PHILLIPS<sup>4</sup>

RECEIVED JULY 31, 1953

In 1931 Blatt<sup>5</sup> showed that isoxazolines gave no methane on treatment with methylmagnesium iodide and on this basis assigned structure I to them. The same year Blatt and Stone<sup>6</sup> showed that isoxazolines derived from substituted chalcones had

(1) This work was supported by a grant from the Research Corporation of New York for the purchase of a Perkin-Elmer 12C infrared spectrometer.

(2) The authors wish to acknowledge the invaluable aid of Mr. Jonas Carroll of the Food and Drug Administration, U. S. Department of Health, Education and Welfare, and the use of their Perkin-Elmer 21 infrared spectrometer.

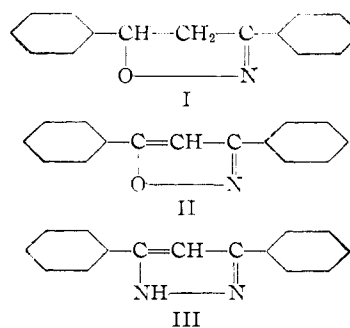
(3) Research Associate in Chemistry, Howard University, Washington, D. C.

(4) In partial fulfillment of the requirements for the master's degree in chemistry.

(5) A. H. Blatt, *THIS JOURNAL*, **53**, 1133 (1931).

(6) A. H. Blatt and J. D. Stone, *ibid.*, **58**, 4189 (1931).

nitrogen attached to what had been the carbonyl carbon atom of the chalcone.

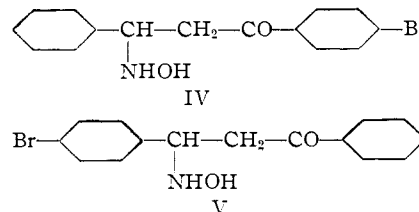


We have now examined the infrared spectra of a number of isoxazolines, their related isoxazoles, and a pyrazole in the belief that additional information as to the structure of isoxazolines would thereby be obtained.

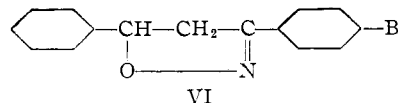
3,5-Diphenyl-, 3-*p*-bromophenyl-5-phenyl-, 3-phenyl-5-*p*-bromophenylisoxazolines and their corresponding isoxazoles all showed strong absorption at  $5.8\mu$ , attributable to the  $-\text{C}=\text{N}-$  grouping, but no absorption in the  $2-9\mu$  region. In contrast, 3,5-diphenylpyrazole shows absorption at  $2.9\mu$  owing to the presence of an  $-\text{NH}-$  grouping. These findings confirm the assignment of structure I to the isoxazolines, and Barnes and Dodson were in error in assigning to 3-*p*-bromophenyl-5-phenylisoxazoline and the corresponding isoxazole the 3-phenyl-5-*p*-bromophenyl structure.<sup>7</sup>

In recent studies by Barnes and co-worker<sup>8</sup> it was found that chalcones with highly hindered carbonyls such as benzalacetomesitylene do not form isoxazolines but yield substituted hydroxylamines instead. They isolated the substituted hydroxylamine hydrochloride which upon rearrangement and hydrolysis<sup>9</sup> yielded benzylmesityl-glyoxal, as Blatt's corresponding methoxy derivatives rearrange and hydrolyze to alpha diketones.

From the isomeric benzal-*p*-bromoacetophenone and *p*-bromobenzalacetophenone we prepared the isomeric hydroxylamino ketones IV and V, respectively, isolating them as their hydrochlorides.



The hydrochlorides of the hydroxylamino ketones IV and V were subjected to treatment with hydroxylamine hydrochloride and excess potassium hydroxide, and they yielded isoxazolines VI and VII, respectively.



(7) R. P. Barnes and L. M. Dodson, *ibid.*, **67**, 132 (1945).

(8) Nancita Robinson, unpublished master's thesis, Department of Chemistry, Howard University, 1949.

(9) A. H. Blatt, *THIS JOURNAL*, **61**, 3494 (1939).