[CONTRIBUTION FROM THE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Ultraviolet Absorption Spectra of Oxazolones and Related Compounds[1]

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Errors in the ultraviolet absorption spectra of substituted oxazolones recently reported by others[2] are pointed out. The effect of solvent on the absorption spectra and on the stability of oxazolones has been studied. Transacylation has now been noted in the preparation of several oxazolones.

The ultraviolet absorption spectra of a variety of substituted oxazolones have been investigated by Schueler and Wang[2] who discussed the effect of substitution in the 2- and 4-positions on the spectra. Schueler and Hanna[3] later compared the spectra of substituted crotonolactones with spectra of oxazolones. Earlier investigations include those of T. Asahina[4] who reported the ultraviolet absorption spectra of a number of compounds including 2-phenyl-4-benzal-5-oxazolone (I), 2-phenyl-4-fural-5-oxazolone and the α-benzamido acids derived from these oxazolones.

Schueler and Wang have reported only a small difference in the absorption spectra of I and 2-methyl-4-benzal-5-oxazolone. But large differences have already been reported in the spectra of certain 2-phenyloxazolones as compared with 2-methyloxazolones.[5,6,7] This discrepancy prompted us to investigate the ultraviolet absorption spectra of a number of compounds which we had prepared in connection with other research being carried out in these laboratories.

Experimental

Preparation of Oxazolones.—Most of the oxazolones were prepared by refluxing for two hours mixtures of the appropriate aldehyde with hippuric acid, sodium acetate and acetic anhydride with mole ratios 1:1:1:10. The iodine-containing oxazolones were prepared by warming the reactants at 100° for only one hour. All oxazolones were isolated either directly from the cooled reaction mixture or after addition of an equal volume of water, and were recrystallized from benzene, benzene–ligroin or ethyl acetate.

Preparation of Substituted Cinnamic Acids and Esters.—The acids and esters were prepared from the oxazolones by the method of Carter and Risser.[8] Water or acetone was used to recrystallize the acids. Ethyl (α-benzamido)-cinnamate was also obtained from a solution containing 5.6 mg. of (I) dissolved in 500 ml. of 95% ethanol which had stood for 21 days at room temperature. Some 430 ml. of this aged solution was concentrated to dryness *in vacuo* at a temperature not exceeding 40° and the residue was recrystallized from ethyl acetate–hexane to yield 3.9 mg. (80% of theoretical yield) of the alcoholysis product, m.p. 145–146° (lit.[8] 147–149°).

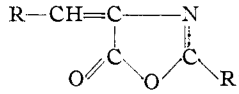
Absorption Spectra.—All spectra were determined with a Beckman quartz spectrophotometer model DU. Unless otherwise stated, all spectra were obtained within 30 minutes after solution of the sample in the appropriate solvent.

Results

Table I presents spectra data for the oxazolones studied, and Table II lists data for some acids and esters derived from the oxazolones. The spectra shown in Fig. 1 illustrate the "spontaneous" as well as the alkali-catalyzed alcoholysis of I, whereas Fig. 2 shows spectra of derivatives of I. Figures 3 and 4 present series of curves illustrating the variation in stability of another oxazolone in different solvents. Figures 5–7 are spectra of pure com-

TABLE I

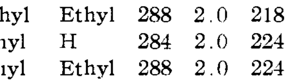
SPECTRAL DATA



Substituents R	R′	Solvent	Principal Max., mμ	$\epsilon \times 10^{-4}$
Phenyl	Methyl	$CHCl_3$	332	2.8
Phenyl	Phenyl	$CHCl_3$	366	3.9
		Ether	360	4.2
4-Fluorophenyl	Methyl	$CHCl_3$	335	2.8[5]
4-Fluorophenyl	Phenyl	$CHCl_3$	368	3.9[5]
2-Chlorophenyl	Methyl	$CHCl_3$	335	2.1
2-Chlorophenyl	Phenyl	$CHCl_3$	370	3.3
4-Chlorophenyl	Methyl	$CHCl_3$	337	2.9
4-Chlorophenyl	Phenyl	$CHCl_3$	370	4.3
		Ether	365	4.2
		95% EtOH	365	4.0
3,5-Diiodo-4-acetoxyphenyl	Methyl	$CHCl_3$	336	2.9
		95% EtOH	332	2.7
3,5-Diiodo-4-(4′-methoxyphenoxy)-phenyl	Phenyl	$CHCl_3$	376	4.2
2-Furyl	Phenyl	$CHCl_3$	390	3.7
4-Dimethylaminophenyl	Phenyl	$CHCl_3$	472	5.5
		Ether	455	5.9

TABLE II

SPECTRAL DATA



$$\begin{array}{l} R—CH=C—NH—CO—R' \\ \qquad\qquad\;\; | \\ \qquad\qquad\;\; CO—O—R'' \end{array}$$

Substituents R	R′	R″	Maxima in 95% ethanol mμ	$\epsilon \times 10^{-4}$	mμ	$\epsilon \times 10^{-4}$
Phenyl	Phenyl	H	279	1.7	222	1.8
Phenyl	Phenyl	Ethyl	282	1.8	222	1.9
2-Chlorophenyl	Phenyl	H	278	1.4	220	2.0
2-Chlorophenyl	Phenyl	Ethyl	279	1.4	220	1.8
4-Chlorophenyl	Methyl	H	284	1.9	217	1.1
4-Chlorophenyl	Methyl	Ethyl	288	2.0	218	1.1
4-Chlorophenyl	Phenyl	H	284	2.0	224	2.0
4-Chlorophenyl	Phenyl	Ethyl	288	2.0	224	1.9
3,5-Diiodo-4-hydroxyphenyl	Methyl	H	298	1.7	245	2.3
2-Furyl	Phenyl	H	311	2.1	228	1.3
2-Furyl	Phenyl	Ethyl	313	2.1	228	1.2

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(1) Part of the work described in this paper was sponsored by the U. S. Atomic Energy Commission.

(2) F. W. Schueler and S. C. Wang, THIS JOURNAL, **72**, 2220 (1950).

(3) F. W. Schueler and C. Hanna, *ibid.*, **73**, 3528 (1951).

(4) T. Asahina, *Bull. Chem. Soc. Japan*, **4**, 202 (1929); **5**, 354 (1930).

(5) E. L. Bennett and C. Niemann, THIS JOURNAL, **72**, 1803 (1950).

(6) E. L. Bennett, Ph.D. Thesis, Calif. Inst. of Tech., Pasadena, Calif., 1949.

(7) S. N. Timasheff and F. F. Nord, THIS JOURNAL, **73**, 2390 (1951).

(8) H. E. Carter and W. C. Risser, *J. Biol. Chem.*, **139**, 255 (1941).

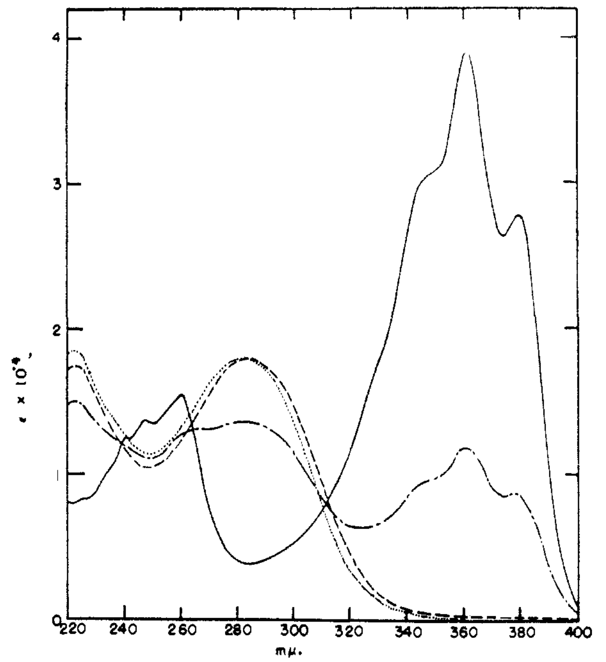

Fig. 1.—Ultraviolet absorption spectra of 2-phenyl-4-benzal-5-oxazolone in 95% ethanol: 30 minutes after solution, ——; 5 days after solution, — — — —; 21 days after solution, - - - - -; and 10 minutes after solution in N/2000 potassium hydroxide in 95% ethanol, ...

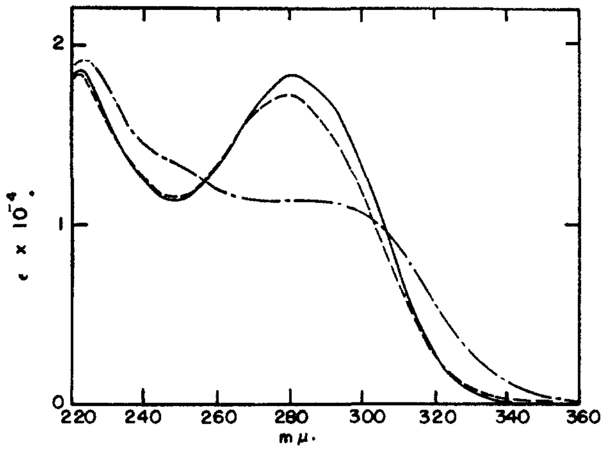

Fig. 2.—Ultraviolet absorption spectra: of ethyl (α-benzamido)-cinnamate in 95% ethanol, ——; α-benzamidocinnamic acid in 95% ethanol, -----; and the α-benzamidocinnamate anion in N/2000 potassium hydroxide in 95% ethanol, — — — —.

pounds,[9] included for the purpose of comparison with spectra reported by Schueler and Wang.[2] Transacylation is illustrated through the spectra presented in Figs. 8 and 9.

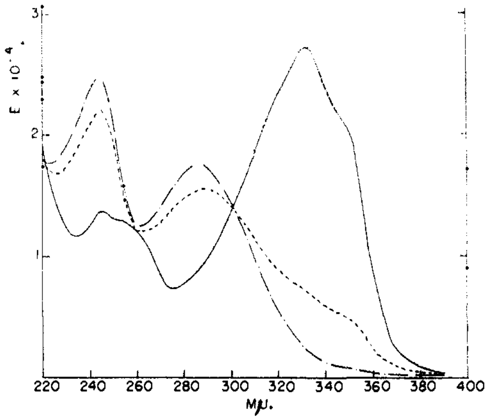

Fig. 3.—Ultraviolet absorption spectra of 2-methyl-4-(3′,5′-diiodo-4′-acetoxybenzal)-5-oxazolone in 95% ethanol: after 30 minutes, ———; 24 hours, — — —; and 48 hours, —·—·—·—.

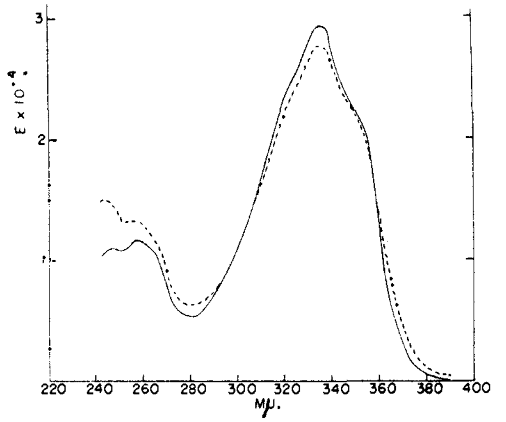

Fig. 4.—Ultraviolet absorption spectra of 2-methyl-4-(3′,5′-diiodo-4′-acetoxybenzal)-5-oxazolone in chloroform: after 30 minutes, ——; 24 hours, — — —.

Discussion

It is evident that most of the spectra reported by Schueler and Wang[2] are not the spectra of oxazolones, and it is most likely that these spectra represent the alcoholysis products of the oxazolones, *i.e.*, substituted ethyl cinnamates. By examination of spectra alone, one cannot rule out the possibility that some hydrolysis product, *i.e.*, substituted cinnamic acid, is present along with alcoholysis product, because the spectra of acid and corresponding ester are so similar. But experiments on the oxazolone I indicate that the alcoholysis product may have been the major constituent, if not the only one, in all cases where the spectra of Schueler and Wang are in disagreement with our spectra.

Figures 1 and 3 show that changes occur in the spectra of oxazolones when these compounds are dissolved in ethanol. The alcoholysis reaction is known to be catalyzed by acids[10] and by bases.[11] We found that the reaction of (I) occurred very rapidly, essentially completely in less than five minutes, in a very dilute solution in 95% ethanol to which potassium hydroxide had been added (ten moles alkali per mole of azlactone); in 95% ethanol alone we observed that the azlactone was half converted to ester in 3–4 days.

It is of interest to note, as shown by consideration of Figs. 1 and 2, that the base-catalyzed solvol-

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(9) The ultraviolet absorption spectra reported by Asahina[1] are qualitatively similar to those reported here, although the fine structure present is not shown. Also, an error appears to have been made in the text; the absorption maximum of (I) is stated to be at 2760 Å. (fig. indicates 362 mμ) and the absorption maximum of 2-phenyl-4-fural-5-oxazolone appears to be at 392 mμ instead of 2550 Å. as stated in the text.

(10) E. Erlenmeyer, *Ann.*, **275**, 8 (1893).

(11) E. Erlenmeyer and W. Stadlin, *ibid.*, **337**, 283 (1904).

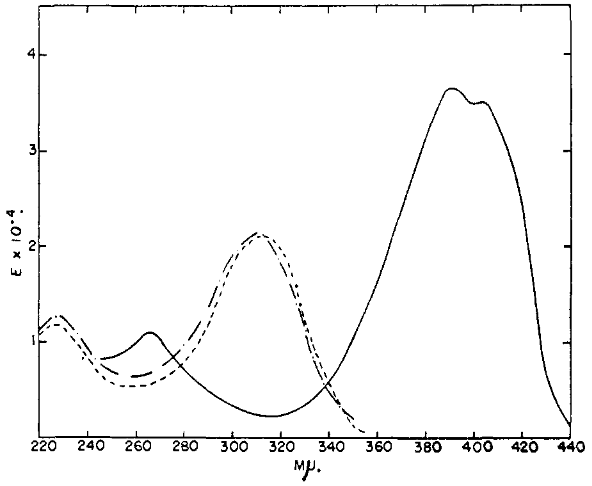

Fig. 5.—Absorption spectra: of 2-phenyl-4-(2′-fural)-5-oxazolone in chloroform, ——; ethyl α-benzamido-β-(2-furyl)-acrylate in 95% ethanol, — — — —; and α-benzamido-β-(2-furyl)-acrylic acid in 95% ethanol, —·—.

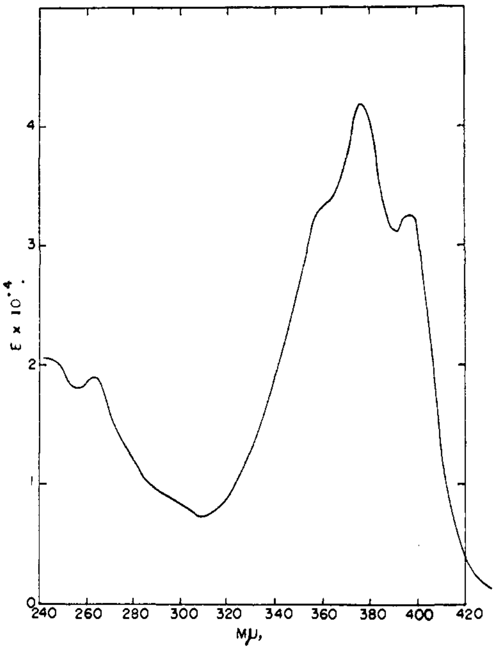

Fig. 6.—Ultraviolet absorption spectrum of 2-phenyl-4-(3′,5′-diiodo-4′-[4″-methoxyphenoxy]-benzal)-5-oxazolone in chloroform.

ysis of the oxazolone yielded only alcoholysis product, with no detectable amount of hydrolysis product. At the same molar concentrations of alkali and organic compound as used for the oxazolone above, α-benzamidocinnamic acid produced the spectrum characteristics of its anion, and ethyl (α-benzamido)-cinnamate produced a spectrum no different from that obtained in the absence of alkali. The spectra of all three alkaline solutions did not change appreciably from the time they were first measured until one day later. Therefore, even in very dilute solutions of oxazolone and alkali in 95% ethanol, alcoholysis proceeds rapidly to substituted ethyl cinnamate without the intermediate formation of substituted cinnamic acid.

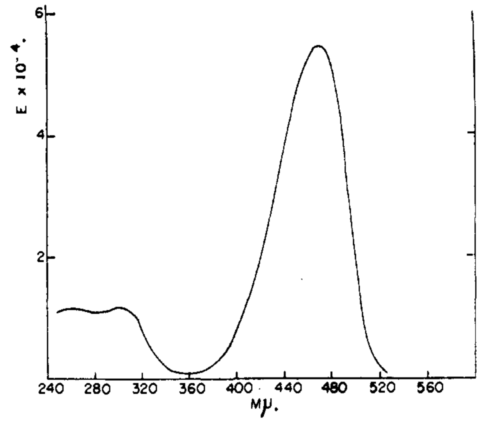

Fig. 7.—Absorption spectrum of 2-phenyl-4-(4′-dimethylaminobenzal)-5-oxazoline in chloroform.

The slow change in spectrum of oxazolone in 95% ethanol to which no alkali had been added reflects formation of the ethyl ester also, as shown by the isolation of pure ethyl (α-benzamido)-cinnamate from the dilute solution of I in 95% ethanol which had been stored for 21 days.

Other experiments indicate that oxazolones are relatively stable in chloroform or ether solutions; only slight changes in spectra are observed in periods up to one month after preparation of solutions when stored under normal laboratory conditions. It is recommended that the spectra of oxazolones be measured in "inert" solvents like chloroform or ether whenever this is possible and not in alcohols.[12]

The change in spectrum of 2-methyl-4-(3′,5′-diiodo-4′-acetoxybenzal)-5-oxazolone when stored in 95% ethanol, Fig. 3, is much more rapid than the change on storage in the spectrum of I, Fig. 1. There is probably an autocatalytic effect here; the 4′-acetoxy group may be removed (probably to form ethyl acetate) leaving an *o,o*-diiodophenol which is rather acidic. In chloroform, Fig. 4, this oxazolone is stable.

We found the spectrum of 2-phenyl-4-(4′-dimethylaminobenzal)-5-oxazolone in chloroform, Fig. 7, to be similar to that reported by Schueler and Wang[2] who used 95% ethanol as solvent. However, they found the main band (475 mμ) to be only about half as intense as we found. A lesser maximum at *ca.* 370 mμ appears in their spectrum but it is completely absent in our spectrum, and this suggests that their solution was not that of a pure azlactone.

The absorption spectra obtained for oxazolones studied show marked similarity; noteworthy is the similarity of the curves obtained for the oxazolones derived from halogen-substituted aldehydes.[5] The substitution of halogen in the 4-benzal group causes a displacement of the absorption maximum toward longer wave lengths. This shift is more for para substitution than for ortho and is more for chlorine substitution than for fluorine. As is to be expected, the substitution of a *p*-dimethylamino group in the aromatic ring of the 4-substituent causes a large

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(12) The ultraviolet absorption spectra show a bathochromic displacement of about 5 mμ when determined in chloroform as compared to spectra obtained in ether or ethanol, as is evident from some data presented in the tables.

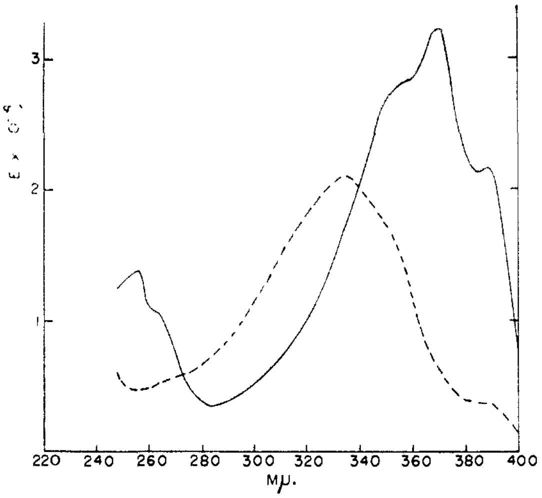


Fig. 8.—Ultraviolet absorption spectra in chloroform of 2-phenyl-4-(2′-chlorobenzal)-5-oxazolone, ——; and 2-methyl-4-(2′-chlorobenzal)-5-oxazolone, m.p. 95–99°, — — —.

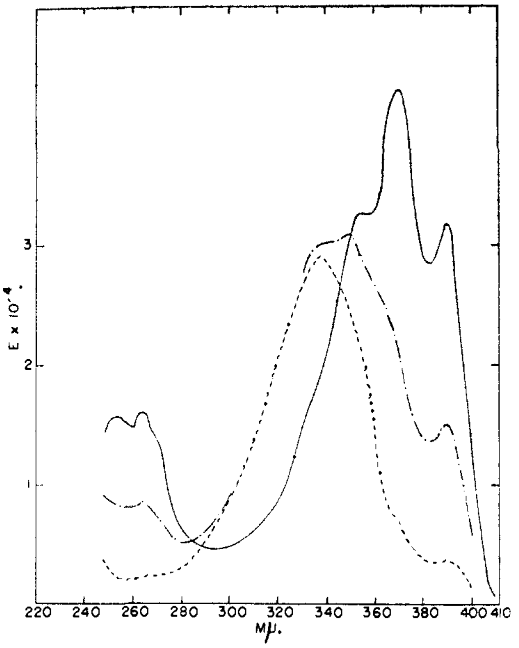
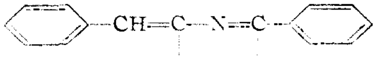


Fig. 9.—Ultraviolet absorption spectra in chloroform: of 2-phenyl-4-(4′-chlorobenzal)-5-oxazolone, ——; 2-methyl-4-(4′-chlorobenzal)-5-oxazolone, m.p. 133–138°, — — —; and crude oxazolone, m.p. 143–175°, —·—·—.

bathochromic and auxochromic effect in the absorption spectrum. The substitution of 2-fural for benzal produces a bathochromic displacement of about 30 mμ; a similar displacement of about 30 mμ (solvent not specified) has been observed when 2-thenal is substituted for benzal.[7]

The positions of the maxima of the phenyl oxazolones studied indicated that the resonating system involved in the absorption of light does include

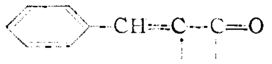


$$C_6H_5—CH{=}C—N{=}C—C_6H_5$$

There is a striking similarity between the shape of the spectra obtained for I and its derivatives and that reported for *trans-trans*-diphenylbutadiene.[13] The presence of a peak or shoulder on each side of the principal absorption maximum is to be noted. There is also some similarity between the data presented herein for oxazolones and that presented in a note by Schueler and Hanna[3] for numerous crotonolactones; this similarity suggests that the latter spectra are truly those of crotonolactones even though they were determined in alcoholic solutions.

The data obtained for oxazolones having the methyl substituent in the 2-position show the expected differences of 2-methyl from the 2-phenyl derivatives. A hypsochromic displacement of about 30 mμ is observed and the peaks on the sides of the main maximum are not observed for the 2-methyl derivatives. The second main peak is not observed in the neighborhood of 240–250 mμ.

The ultraviolet absorption spectra of the acids and esters derived from several of the oxazolones exhibit absorption maxima at much shorter wave lengths (50–100 mμ) than the parent compound,[4] but only small differences are to be noted in the spectra of the free acids as compared to the corresponding ester (*cf.* Table II and Figs. 2 and 5). Substitution of α-acetamido for α-benzamido in α-benzamido-4-chlorocinnamic acid produces no significant change in the absorption maxima in the region of 284 mμ, but as would be expected, the spectra at lower wave lengths are different. The absorption data obtained for these compounds are similar to those obtained for α,β-unsaturated ketones[14] and are consistent with the idea that the following is the principal resonating system



$$C_6H_5—CH{=}C—C{=}O$$

Transacylation in the Erlenmeyer–Plöchl synthesis appears to be a general reaction. It was previously observed when the reaction was carried out at refluxing temperatures,[5] and was then observed in the preparation of 2-phenyl-4-(2′-chlorobenzal)-5-oxazolone and 2-phenyl-4-(4′-chlorobenzal)-5-oxazolone. The conditions used above were more drastic than those usually used; a higher temperature was purposely used to enhance any tendency toward transacylation. Further study is necessary to ascertain if transacylation did not occur in those cases in which it was not observed. As observed here, transacylation is the replacement of a benzoyl group by an acetyl group. Since the acetyl derivative is generally more soluble in the usual solvents for recrystallization than is the benzoyl derivative, isolation of the pure acetyl derivative is difficult, but it has been accomplished chromatographically.[5]

In the present work the extent of transacylation is estimated from the ultraviolet absorption spectrum of the crude reaction product obtained in the preparation of the 4′-chlorobenzal oxazolone, Fig. 9. One-half of the crude product appears to be the 2-methyl derivative. The ultraviolet absorption data presented for 2-methyl-4-(2′-chlorobenzal)-5-oxazolone and for 2-methyl-4-(4′-chlorobenzal)-5-

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(13) J. H. Pinckard, B. Wille and L. Zechmeister, THIS JOURNAL, **70**, 1938 (1948).

(14) A. L. Wilds, L. W. Beck, W. J. Close, C. Djerassi, J. A. Johnson, Jr., T. L. Johnson and C. H. Shunk, *ibid.*, **69**, 1985 (1947).

oxazolone were obtained from these compounds isolated by fractional crystallizations as by-products from the preparation of the 2-phenyl derivatives. In each case, there is still about 5–15% of the 2-phenyl derivative present. The effect of variables such as time of heating and temperature on the rate of transacylation can now be readily investigated since the reaction has been shown to occur with readily available compounds as well as with the more difficultly obtainable fluorobenzaldehyde azlactones.

Acknowledgment.—The authors wish to express their appreciation to Professor Melvin Calvin for his interest in the problem.

Berkeley, California

[Contribution No. 1098 from the Sterling Chemistry Laboratory, Yale University]

Experiments in the 1,2-Di-(γ-pyridyl)-ethane Series[1]

By Ernst D. Bergmann,[2] Francis E. Crane, Jr., and Raymond M. Fuoss

Received June 16, 1952

1,2-Di-(γ-pyridyl)-ethane and its methiodide are readily oxidized to the corresponding ethylene derivatives. The two bases form mixed crystals, as do their salts. The ethylene absorbs strongly at 295 mμ, where stilbene has its absorption. A pronounced bathochromic shift occurs on methiodation; the bismethiodide of the ethylene absorbs at 315 mμ, approximately where diphenylbutadiene absorbs. Both methiodides show a much stronger absorption at 225 mμ than tetraalkylammonium iodides; furthermore, the (solid) ethane methiodide is yellow and the ethylene methiodide is ruby-red, while the methobromides and methonitrates of both bases are colorless. A marked deformation of the iodide ion by the pyridinium ion is therefore indicated. Chloranil forms a brown-violet addition compound with 1,2-di-(γ-pyridyl)-ethane, which peptizes in water.

The immediate purpose of the present investigation was the elucidation of a number of puzzling observations made in the course of the preparation of 1,2-di-(γ-pyridyl)-ethane and -ethylene[3] dimethiodides. When the ethane compound was quaternized and the product subjected to fractional crystallization, vividly colored fractions, ranging from yellow to ruby-red, were obtained; in particular, upon prolonged standing, crystallizates of intensely red color were observed. Investigation has shown that the red product was the dimethiodide of the *ethylene* and that the color variation was due to the presence of varying amounts of the unsaturated quaternary salt mixed with the dimethiodide of the saturated compound. This behavior was traced to two causes. First, 1,2-di-(γ-pyridyl)-ethane and -ethylene cannot be separated completely by crystallization, as described by Thayer and Corson[3]; the bases, as well as their methiodides, appear to form mixed crystals, in the same manner as dibenzyl and stilbene.[4] Incidentally, this seems to prove that the ethylene is the *trans*-form as *cis*-isomers are known not to give mixed crystals with the corresponding saturated compounds. Second, the saturated dimethiodide, when its solution is exposed to air, is gradually dehydrogenated to the unsaturated quaternary salt. This oxidation is undoubtedly due to the particular nature of the 1,2-diarylethane compounds, which involves a large contribution from hyperconjugated forms.[5] Thayer and Corson[3] have already commented on the relative ease of the dehydrogenation of the ethane. It has now been shown that the ethane reacts smoothly with N-bromosuccinimide, giving the hydrobromide of 1,2-di-(γ-pyridyl)-ethylene.[6] Another significant observation was made: when the ethane was added to a solution of chloranil in xylene, a dark-brown, quinhydrone-like compound precipitated. This suggests that the ethane has the character of a hydroquinone, the quinone form obviously being the 1,2-di-(γ-pyridyl)-ethylene.[7,8]

Spectral analysis provided an accurate method of characterizing the various compounds. Furthermore, it was found that the solubilities of the two dimethiodides in nitroparaffins are so different that they can be prepared in quite pure form by recrystallization of the ethane compound from nitromethane, in which the ethylene dimethiodide is only very slightly soluble, while the latter can be recrystallized from 1-nitropropane. The former gives well-shaped yellow prisms, the latter fine brown-red needles. Figure 1 shows the two spectra; it also includes an example of an "orange" salt which was obtained in the course of a lengthy (and unsuccessful) fractional crystallization of the ethane dimethiodide. The ethylene dimethiodide has a very sharp maximum at 315 mμ (ε 41,000), while the ethane salt has no absorption in this region, but a maximum at 255 mμ (ε 8,000). The visible spectrum of both methiodides shows no distinct bands but a gradually decreasing absorption as one proceeds from 360 to 500 mμ (ethane, ε 16.4 to 0.097; ethylene, ε 294 to 16.1; Fig. 2). It is surprising that the red ethylene bismethiodide is only yellow in aqueous solution.

The shift in the ultraviolet spectra of the ethane

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(1) Paper No. 34 of Project NR 002-054 of the Office of Naval Research.

(2) Weizmann Institute of Science; Woodward lecturer, Yale University, March, 1952.

(3) H. I. Thayer and B. B. Corson, This Journal, **70**, 2331 (1948).

(4) G. Bruni, quoted by G. Wittig, "Stereochemie," Akademische Verlagsgesellschaft, Leipzig, 1930, p. 318; P. Pascall and L. Normand, *Bull. soc. chim.*, [4] **13**, 154 (1913).

(5) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc, New York, N. Y., 1941, p. 116.

(6) For the reaction of *sym*-diarylethanes with N-bromosuccinimide, see R. A. Barnes, This Journal, **70**, 145 (1948); E. Bergmann and J. Szmuszkowicz, *ibid.*, **73**, 5153 (1951).

(7) For the dehydrogenation of *sym*-diarylethanes by chloranil, see E. Buchta and W. Kallert, *Ann.*, **573**, 227 (1951).

(8) For the dehydrogenation of hydrogenated heterocyclic compounds by chloranil, see Ng. Ph. Buu-Hoi, Ng. Hoan and Ng. D. Xuong, *J. Chem. Soc.*, 279 (1952).