Anal. Calcd. for $C_{10}H_8O_3$: C, 68.16; H, 4.58. Found: C, 67.82; H, 4.68.

The absorption spectra of the chromone and of 2-methylchromone are shown in Fig. 2.

The benzyl group of the benzyloxymethyl chromone could also be removed by treatment with hot, concentrated hydrochloric acid. An attempt to bring about the debenzylation by catalytic hydrogenation over 10% Pd–charcoal was unsuccessful: the uptake of hydrogen showed no distinct change after one mole had been absorbed, and no definite product was isolated when the experiment was interrupted at that point.

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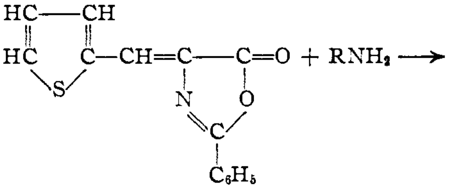
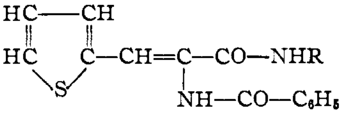
Aminolysis and Alcoholysis of a Thiophene Azlactone

BY ROBERT J. GIBBS,[1] SERGE N. TIMASHEFF AND F. F. NORD

When studying the interaction[2] of egg albumin with 2-phenyl-4-(2-thenal)-5-oxazolone (I) recently synthesized[3,4] from 2-thenaldehyde, it was observed that the azlactone reacts readily with the amino groups of the protein. It was therefore decided to investigate the behavior of the azlactone in the presence of a variety of compounds containing a primary amino group, inasmuch as this is by far the predominant group of this type in the protein. Under the experimental conditions employed, the expected[5] reaction is



I



II

Applying an earlier method,[6] it was possible to react I stoichiometrically with *n*-octylamine in ethanol to obtain the *n*-octylamide of α-benzamido-β-2-thienylacrylic acid (II, R = C_8H_{17}) in quantitative yield.[2] Similarly, 1-phenyl-2-aminopropane, 1-(2-thienyl)-2-aminopropane and 2-aminothiazole produced the expected amides, also in excellent yield. However, cytosine was found to be unreactive.

Aniline was treated in two ways, with ethanol and excess aniline, respectively, as solvents. The yellow crystalline substance obtained, however, was found to be merely the unreacted azlactone with some aniline physically adsorbed to it. This finding is of special interest, in view of the fact that aniline easily reacts with similar benzene analogs of the thiophene azlactone,[6] using the same two methods as above.

With 2-aminopyridine, and its 3- and 6-methyl analogs, reaction products were obtained which did not analyze properly for the respective amides. Further investigation showed that all three pyridines gave the same product, *i.e.*, the ethyl ester of the acrylic acid. This compound has been previously prepared[7] by treating the azlactone with ethanol in the presence of sodium ethoxide. The chemical identity of the three pyridine reaction products with the ethyl ester was demonstrated in three ways: (1) the analyses for carbon, hydrogen and nitrogen were within the range of the ethyl ester; (2) the melting points were the same as reported[7] for the ethyl ester, and mixed melting points of the products with one another, and with an authentic sample of the ester, gave no change in melting point; (3) ultraviolet spectra of the three products were sensibly identical, and fitted that of the ester (see Table I).

TABLE I

ABSORPTION MAXIMA AND MOLECULAR EXTINCTION COEFFICIENTS OF THE OXAZOLONE AND ITS DERIVATIVES

	Maxima	
Compound	mμ	$\epsilon \times 10^{-3}$
2-Phenyl-4-(2-thenal)-5-oxazolone[a]	269–270	15.1
	394	36.6
α-Benzamido-β-2-thienylacrylic acid	227	13.8
	306–307	14.9
B-t-acrylic acid methyl ester	Below 233	..
	315	18.8
B-t-acrylic acid ethyl ester[b]	Below 233	..
	315	18.8
B-t-acrylic acid ethyl ester[c]	229	13.9
	314	19.2
B-t-acrylic acid ethyl ester[d]	228–229	14.1
	314	19.4
B-t-acrylic acid ethyl ester[e]	228–229	14.1
	314	19.4
B-t-acrylic acid thiazolyl amide	223	16.4
	329–330	25.7
B-t-acrylic acid phenylisopropyl amide	230	15.3
	309	17.3
B-t-acrylic acid thienylisopropyl amide	230	18.0
	309–310	14.7
B-t-acrylic acid octyl amide	230	15.0
	309	19.2

[a] Ref. 3c. [b] Prepared using sodium ethoxide. [c] Prepared using 2-aminopyridine. [d] Prepared using 2-amino-3-methylpyridine. [e] Prepared using 2-amino-6-methylpyridine. B-t refers to α-benzamido-β-2-thienyl.

In the present case, it is obvious that the pyridineamines, being strong bases, act catalytically on the alcoholysis of the azlactone, so much so that the ester is formed in preference to the expected amide. However, an investigation of the available literature has disclosed no other case where alcoholysis of an azlactone occurred in preference to aminolysis. In fact, alcohols are often used as solvents for the latter reaction.[5]

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(1) Predoctoral fellow of the Atomic Energy Commission.

(2) S. N. Timasheff and F. F. Nord, *Arch. Biochem. Biophys.*, **31**, 320 (1951).

(3) (a) G. Barger and A. P. T. Easton, *J. Chem. Soc.*, 2102 (1938); (b) B. F. Crowe and F. F. Nord, *Nature*, **163**, 876 (1949); (c) B. F. Crowe and F. F. Nord, *J. Org. Chem.*, **15**, 81 (1950).

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

(5) H. E. Carter, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 198.

(6) C. Gränacher and G. Gulbas, *Helv. Chim. Acta*, **10**, 819 (1927).

(7) B. F. Crowe and F. F. Nord, *J. Org. Chem.*, **15**, 1177 (1950).

Following the usual method,[8] the reaction of I with leucine, and with phenylalanine, was attempted. In each case there was obtained a yellow oil which could not be crystallized from ethanol, dioxane, acetone or acetic acid. Further attempts at purification were abandoned.

Of all the amides formed, that with *n*-octylamine was most easily produced, while 2-aminothiazole reacted least readily. The pyridine-catalyzed alcoholysis proceeded more slowly than did the reactions of the propylamines. In every case where a reaction occurred, a quantitative yield was obtained.

The ultraviolet absorption spectra of a series of thiophene azlactones[3c] and rhodanines[7] having been previously determined, it was of interest to study the effect of various substituent groups on the ultraviolet absorption spectra of the amides and esters of α-benzamido-β-2-thienylacrylic acid. From the absorption curves shown on Fig. 1 and the data presented in Table I, it can be seen that the opening of the oxazole ring of the azlactone results in a shifting of the peaks to lower wave lengths and a diminution in the absorption intensity. Esterification or amidation of the acrylic acid, however, leads to a bathochromic shift in both peaks. Furthermore, it is of interest to note that the introduction of a thiazole ring produces a rise in the molecular extinction coefficients, the absorption maxima remaining, however, in the lower region.

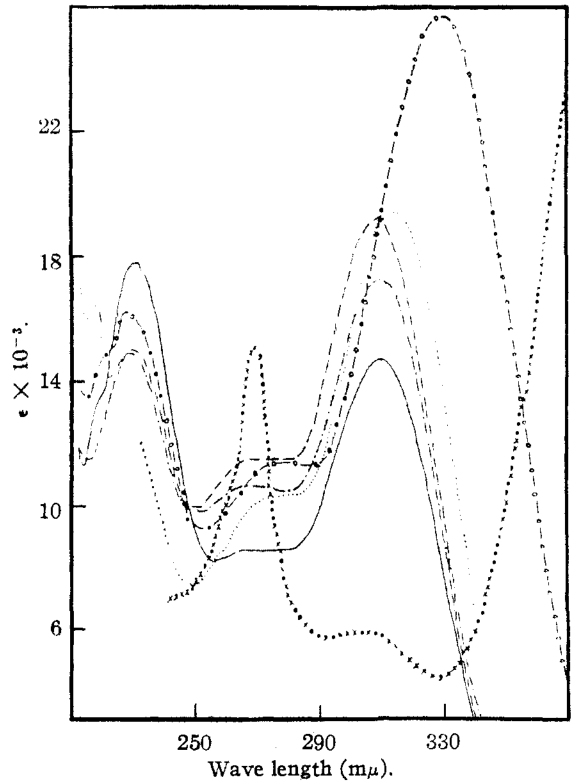

Fig. 1.—Ultraviolet absorption spectra of thiophene azlactone and derivatives: xxxxxx, thiophene azlactone; ......, acrylic acid ethyl ester; - - - -, *n*-octyl amide (R = C_8H_{17}); -O-O-, thiazolyl amide (R = C_3H_2NS); --·--·-, phenylisopropyl amide (R = $C_6H_5CH_2CH(CH_3)$); —, thienylisopropyl amide (R = $C_4H_3SCH_2CH(CH_3)$).

Experimental

Preparation of Acrylic Acid Amides.—To 1 g. of the amine was added a stoichiometric amount of azlactone, and the mixture was refluxed in 30 ml. of ethanol for three hours. On cooling, the addition of water caused the precipitation of the amide, which was recrystallized three times from ethanol. The propyl amides were further recrystalized from benzene. 1-Phenyl-2-aminopropane yielded white crystalline 1-phenylisopropyl-α-benzamido-β-2-thienylacrylamide, m.p. 86.5–87° (uncor.).

Anal. Calcd. for $C_{23}H_{22}O_2N_2S$: C, 70.74; H, 5.68; N, 7.17. Found: C, 70.50; H, 5.75; N, 7.06.

1-(2-Thienyl)-2-aminopropane yielded white crystalline 1-(2-thienyl)-isopropyl-α-benzamido-β-2-thienylacrylamide, m.p. 163.5–164°.

Anal. Calcd. for $C_{21}H_{20}O_2N_2S_2$: C, 63.61; H, 5.08; N, 7.07. Found: C, 63.61; H, 4.96; N, 7.08.

2-Aminothiazole yielded white crystalline 2-thiazolyl α-benzamido-β-2-thienylacrylamide, m.p. 220–220.5°.

Anal. Calcd. for $C_{17}H_{13}O_2N_3S_2$: C, 57.44; H, 3.69; N, 11.82. Found: C, 57.56; H, 3.53; N, 11.80.

Cytosine and aniline gave no amide by the above method, nor did the latter when excess aniline was used as solvent. The *n*-octylamide was prepared as before.[2]

Alcoholysis of Thiophene Azlactone.—2.5 g. (0.01 mole) of I was refluxed for one hour in ethanol, in the presence of 1 g. of 2-aminopyridine (or its 3- or 6-methyl analog). On cooling, the addition of water precipitated the ester, which was recrystallized three times from ethanol. A quantitative yield was obtained of white needles of ethyl α-benzamido-β-2-thienylacrylate, m.p. 177.5–178°.

Ultraviolet Absorption Spectra.—These measurements were made with a Beckman quartz spectrophotometer, model DU, using ethanol as the solvent.

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[8] M. Bergmann and A. Miekeley, *Ann.*, **458**, 40 (1927).

The Reaction of Some Tetrasubstituted Silanes with *n*-Butyllithium

BY HENRY GILMAN AND HOWARD HARTZFELD

It has been shown[1] that when triphenylsilanol, tri-*p*-tolylsilanol, diphenyl-*p*-tolylsilanol or hexaphenyldisiloxane is refluxed with *n*-butyllithium in ether, there is cleavage of a carbon-to-silicon bond, whereas in the case of tri-1-naphthylsilanol, there is no cleavage. In that publication it was shown that under the same conditions there is no cleavage of a carbon-to-silicon bond in any of a number of tetraaryl- and mixed arylalkylsilanes of the type R_4Si. However, it has been found[2] that certain tetrasubstituted silanes are readily cleaved by potassium hydroxide. The present studies were made in order to determine whether some of the tetrasubstituted silanes which were most readily cleaved by potassium hydroxide might also be cleaved by *n*-butyllithium.

Accordingly, triphenyl-(phenylethynyl)-silane

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[1] H. Gilman, R. A. Benkeser and G. E. Dunn, THIS JOURNAL, **72**, 1689 (1950).

[2] Unpublished studies by Dr. L. S. Miller. See, also, L. H. Sommer, L. J. Tyler and F. C. Whitmore, THIS JOURNAL, **70**, 2872 (1948); J. L. Speier, B. F. Daubert and R. R. McGregor, *ibid.*, **70**, 1117 (1948); E. Larsson and L. O. Knopp, *Acta Chem. Scand.*, **1**, 268 (1947) [*C. A.*, **42**, 5416 (1948)]; A. Bygden, *J. prakt. Chem.*, **96**, 86 (1917); F. S. Kipping, *J. Chem. Soc.*, **125**, 2291 (1924).