The structure of *cis*-III was confirmed by isomerization to *trans*-III, m.p. 121–122°, in 100% yield by treatment with iodine in benzene for ten days. Recrystallization of the product gave an 87% yield of *trans*-III, m.p. 123–124°. A mixed m.p. with an authentic sample showed no depression. An attempt to effect the isomerization of *cis*- to *trans*-III by the method of Price and Meister[21] was unsuccessful.

Addition of bromine in carbon disulfide at 0° to the chromatographed *cis*-III yielded 23% of *meso*-stilbene dibromide, m.p. 238° (dec.), and 72% of crude *dl*-stilbene dibromide, m.p. 100–107°, which on recrystallization from absolute ethanol gave a 50% yield of colorless plates, m.p. 111–112.5°.[18]

Preparation and Reactions of the Lithium Reagent from *trans*-I (a) **Carbonation to** *trans*-II.—*trans*-I was prepared by the thermal isomerization of a mixture of *cis*- and *trans*-I.[22] The lithium reagent was prepared from 0.75 g. of *trans*-I and carbonated by the procedure described above for *cis*-I. In this case the addition of aniline to the acidic products in benzene gave 0.57 g. (0.0018 mole, 62%) of the anilinium salt of *trans*-II, m.p. 128.5–129.5°. A mixed m.p. with an authentic sample gave no depression. No *cis*-II could be obtained.

(b) **With Methanol.**—The lithium reagent from 0.90 g. of *trans*-I, prepared as described above for *cis*-I, was found to give, on treatment with methanol, 0.61 g. (0.0034 mole, 97%) of crude *trans*-III, m.p. 80–106°. Recrystallization from methanol yielded 0.37 g. (0.0021 mole, 58%), m.p. 121.5–123°; mixed m.p. with an authentic sample, 122–124°.

Carbonation of the Lithium Reagent from α-**Bromostyrene** (IV).—IV, b.p. 76–77° (10 mm.), n^{25}_{D} 1.5869, was prepared in 50% yield from styrene dibromide by the method of Glaser[23] and purified by distillation under nitrogen. When 1.34 g. (0.0073 mole) of IV was allowed to undergo a lithium–halogen exchange with butyllithium in ether at −35° for seven minutes and then poured on Dry Ice, 0.59 g. (0.0040 mole, 55%) of crude α-carboxystyrene, m.p. 96–102.5°, was obtained. Recrystallization from 80% ethanol raised the m.p. to 105.5–106.5° (lit.[24] m.p. 106–107°). This compound was converted to the dibromide, m.p. (from chloroform) 114–115.5° (lit.[24] 115–116°) in excellent yield by treatment with bromine in carbon disulfide. No phenylpropiolic acid could be found in the carbonation products.

Carbonation of the Lithium Reagent from ω-Bromostyrene (VI).—A mixture of *cis*- and *trans*-VI obtained by distilling commercial VI (b.p. 105–107° (25 mm.)) was employed. A solution of butyllithium in ether was added to a solution of VI in ether at −35° over a period of 4.5 minutes and, after an additional 1.5 minutes poured onto Dry Ice. During the reaction the temperature rose to 0° and then fell again to −13°. Addition of aniline to a benzene solution of the resultant acids gave 0.81 g. (0.0034 mole, 45% yield) of the anilinium salt, m.p. 108.5–109.5°, of phenylpropiolic acid (VII). The salt was converted to VII, m.p. 136.5–137.5°. The *p*-nitrobenzyl ester melted at 82–83° (lit.[25] m.p. 83°). No *cis*- or *trans*-cinnamic acid could be isolated.

When the reaction of VI with butyllithium was carried out for a total of six minutes at −55° the only acidic product was a 9% yield of VII. Thirty minutes at −55° gave a 30% yield of VII as the only acidic product.

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[21] C. C. Price and M. Meister, THIS JOURNAL, **61**, 1595 (1939). Compare D. C. Downing and G. F Wright, *ibid.*, **68**, 141 (1946).

[22] J. Wislicenus and F. Seeler, *Ber.*, **28**, 2693 (1895).

[23] C. Glaser, *Ann.*, **154**, 137 (1870).

[24] R. Fittig and C. Wurster, *ibid.*, **195**, 149 (1879).

[25] E. E. Reid, THIS JOURNAL, **39**, 133 (1917).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Ultraviolet Absorption Spectra of 2-Thienyl Ketones[1]

BY H. HARRY SZMANT AND ARTHUR J. BASSO

The ultraviolet absorption spectra of seventeen 2-thienyl ketones are reported and discussed. Included in this study are nine new compounds eight of which represent the thiophene analogs of the chalcone structure.

In this paper we wish to report the results of the study of the ultraviolet spectra of a number of 2-thienyl ketones. These compounds are of interest since they provide an opportunity for comparison with the analogous ketones derived from benzene.

Experimental

The ultraviolet spectra were determined by means of a Beckman DU quartz spectrophotometer. The solvent was 95% ethanol. The source references, physical constants and spectral results[2] are listed in Table I.

Discussion of Results

All of the simple 2-thienyl ketones reported in this study (except compound no. 7, Table I) exhibit two maxima which appear to be related to the 260 and 285 mμ bands of 2-thienyl methyl ketone.[3] The introduction of a chlorine or a methyl group into the 5-position (compounds 2 and 5) causes greater bathochromic and hyperchromic effects in the 285 mμ band than the 260 mμ band. It is probable that the electronic transitions responsible for the 285 mμ band in the ketones reported in this paper are similar to the electronic transitions which produce the 282 mμ maximum of 2-phenylthiophene[4] and the 272 mμ maximum of 2-vinylthiophene.[5] The two bands in the 2-thienyl ketones seem also to correspond to the 255 and 275 mμ bands of 2-furyl ketones.[6]

The remarkable spectral difference between the 4-methyl- or 5-methyl-2-acetothienones and the 3-methyl isomer suggests an electronic interaction between the methyl and carbonyl groups in the latter compound. A hyperconjugation phenomenon with hydrogen bonding in the excited state[7] is a likely explanation for the spectral behavior of 3-methyl-2-acetothienone.

Among the relatively simple 2-thienyl ketones prepared in this study was 1,3-di-(2-thenoyl)-2-*p*-chlorophenylpropane (compound 4). The absorption spectrum of this compound confirmed the structure proposed on the basis of the analytical data since it showed the presence of the maxima

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[1] Presented before the Organic Division at the September, 1950, Meeting of the American Chemical Society at Chicago.

[2] The complete spectral curves are contained in the M.S. thesis of A. J. B., Duquesne University, June, 1950.

[3] Abe Shigehiro (*J. Chem. Soc. Japan*, **59**, 1117 (1938)) reported a single maximum for this compound at 266 mμ. It is noteworthy that the maximum of 2-furyl methyl ketone reported in the same paper (267 mμ) also does not agree with a recent determination (275 mμ reported by Raffauf, THIS JOURNAL, **72**, 753 (1950)).

[4] B. Elpern and F. C. Nachod, *ibid.*, **72**, 3379 (1950).

[5] M. Jackman, *et al.*, *ibid.*, **71**, 2301 (1949).

[6] R. F. Raffauf, *ibid.*, **72**, 753 (1950).

[7] (a) Compare the discussion of the spectra of 2-nitrophenyl phenyl sulfide and of *o*-nitrotoluene by Koch (*J. Chem. Soc.*, 387 (**1949**); (b) H. H. Szmant and H. J. Planinsek, THIS JOURNAL, **72**, 4981 (**1950**).

TABLE I

2-THIENYL KETONES

No.	RCOR′ R	R′	Source[a]	M.p., °C.[b] (lit.)	Absorption maxima λ (mμ)	ε × 10⁻⁴	λ′ (mμ)	ε′ × 10⁻⁴
1	2-Thienyl	Methyl	1	77_4[c] ($77–78_4$)[d]	285	0.56	260	0.78
2	2-(5-Chlorothienyl)	Methyl	1	$95–96_7$[c] ($95–96_7$)[d]	292	1.13	264.5	0.87
3	2-Thienyl	Phenyl	1	143_4[c] ($143–144_4$)[d]	293	1.33	263	1.29
4	1,3-Di-(2-thenoyl)-2-*p*-chlorophenylpropane		2	110–112 (–)	285	1.15	263	1.45
5	2-(5-Methylthienyl)	Methyl	1	[e]	294	1.14	263–264	0.94
6	2-(4-Methylthienyl)	Methyl	1	[e]	295–297	0.63	261	.99
7	2-(3-Methylthienyl)	Methyl	1	[e]	273–274	1.26	...	..
8	2-Thienyl	Styryl	3	81–82 (82)[f]	320	1.93	...	..
9	2-Thienyl	*m*-Trifluoromethylstyryl	3	121–122 (–)[g]	314	2.31	230	.64
10	2-(5-Chlorothienyl)	Styryl	3	103–105 (–)[h]	328	2.10	260	.97
11	2-(5-Methylthienyl)	Styryl	3	93–96 (–)[i]	326	1.73	252	.71
12	2-(4-Methylthienyl)	Styryl	3	102–104 (–)[j]	326	1.78	245	.66
13	2-(3-Methylthienyl)	Styryl	3	43–45 (–)[k]	321	2.65	232	.87
14	2-Thienyl	*p*-Chlorostyryl	3	133.5 (–)[l]	328	2.58	245	.70
15	2-Thienyl	2,4-Dichlorostyryl	3	119–120 (–)[m]	321	1.81	245	.84
16	2-Thienyl	3,4-Dichlorostyryl	3	149–151 (–)[n]	322	2.01	245	.98
17	2-Thienyl	2-Furylvinyl	3	71 (70–71)[f]	353	2.43	243	.56

[a] Source references: (1) Socony–Vacuum Co. (2) Prepared in 60% yield by the condensation of 4.473 g. of 2-thieny methyl ketone and 5.0 g. of 2-chlorobenzaldehyde in 30 ml. of 50% ethanol in the presence of 1 ml. of 10% sodium hydroxide. *Anal.* Calcd. for $C_{19}H_{15}O_2S_2Cl_2$: C, 60.87; H, 4.03. Found: C, 60.73; H, 3.97. (3) The styryl ketones were prepared in 82–95% yields by the condensation of the appropriate aldehydes with the 2-acetothienones. Equimolar quantities of the aldehydes (solid aldehydes were first dissolved in a minimum of warm ethanol) were added to a 60% ethanol solution of the ketone (1.5–4.5 g.) containing approximately 0.5 ml. of 10% sodium hydroxide. The reaction mixtures were mechanically stirred at 0° for two hours and placed in an ice-chest until the products crystallized from solution. The products were crystallized to a constant melting point from ethanol. [b] All melting points are uncorrected. Analyses by the Micro-analytical Laboratory, University of Pittsburgh. [c] Boiling point; subscript indicates pressure in mm. [d] Hartough and Kosak, THIS JOURNAL, **69**, 1015 (1947). [e] A small sample of the pure ketone supplied by the Socony–Vacuum Co. was distilled and the middle-cut was collected. [f] Weygand and Strobelt, *Ber.*, **68B**, 1839 (1935). [g] *Anal.* Calcd. for $C_{14}H_9OSF_3$: C, 59.56; H, 3.21. Found: C, 59.35; H, 2.98. [h] *Anal.* Calcd. for $C_{13}H_9OSCl$: C, 62.77; H, 3.64. Found: C, 62.55; H, 3.44. [i] *Anal.* Calcd. for $C_{14}H_{12}OS$: C, 73.65; H, 5.29. Found: C, 73.98; H, 5.20. [j] *Anal.* Calcd. for $C_{14}H_{12}OS$: C, 73.65; H, 5.29. Found: C, 73.60; H, 5.09. [k] *Anal.* Calcd. for $C_{14}H_{12}OS$: C, 73.65; H, 5.29. Found: C, 73.87; H, 5.01. [l] *Anal.* Calcd. for $C_{13}H_9OSCl$: C, 62.77; H, 3.64. Found: C, 63.04; H, 3.70. [m] *Anal.* Calcd. for $C_{13}H_8OSCl_2$: C, 55.13; H, 2.84. Found: C, 55.10; H, 3.01. [n] *Anal.* Calcd. for $C_{13}H_8OSCl_2$: C, 55.31; H, 2.84. Found: C, 55.31; H, 2.92.

of 2-thienyl methyl ketone in essentially identical positions, and with very nearly double values for the extinction coefficients.

The spectrum of 2-thienyl styryl ketone exhibits but one distinct maximum at 320 mμ (ε 19,200). This band is analogous to that found in chalcones (310 mμ)[8] and the bathochromic shift in the maximum of the 2-thienyl styryl ketone, when compared to the benzene analog (chalcone), is explained in terms of the greater electron donating power of the thiophene ring as compared with benzene. A similar bathochromic displacement can be achieved in the chalcone structure by the presence of an electron donating group in the appropriate position; thus, 4-phenoxychalcone also has a maximum in the 320 mμ range.[8]

The spectra of the chalcones often exhibit maxima which are subject to satisfactory interpretations in terms of electronic oscillations in "isolated" portions of the conjugated system, *i.e.*, partials.[8,9] One of the partials expected in the 2-thienyl styryl ketone structure would be the result of the independent resonance of the 2-thienyl carbonyl group. All of the 2-thienyl styryl ketones investigated in this study exhibit secondary maxima in the range of 240–260 mμ (ε 5000–9000) and it appears that these secondary absorption maxima result from the independent absorption of the 2-thienyl carbonyl group. In the parent compound the secondary maximum at 250 mμ (ε 5400) is hardly discernible, but it becomes quite prominent when substituents are present which either aid the resonance of the 2-thienyl carbonyl unit or which dampen the participation of the styryl group in the resonance of the whole molecule. The principal maxima of the 4-chloro-, 3,4-dichloro- and 2,4-dichlorostyryl 2-thienyl ketones are at 328, 322 and 321 mμ, respectively. Thus, the bathochromic displacements of the 320 mμ band of the parent compound become smaller as the negative inductive effect of the chlorine atoms counteracts the positive electromeric effect. In all three compounds there are found the above mentioned secondary maxima at 245 mμ, and their intensity *increases* parallel with the increasing negative inductive effect of the chlorine atoms.

The introduction of the strongly electron withdrawing trifluoromethyl group in the phenyl group of 2-thienyl styryl ketone (compound 9) causes a hypsochromic shift in the 320 mμ band of the parent ketone. The polarization of the styryl group in the direction of the trifluoromethyl group presumably introduces a partial positive charge on the carbon atom adjacent to the carbonyl group and this would tend to inhibit the resonance of the 2-thienyl carbonyl partial. Thus, it is not surprising that the secondary maximum undergoes in this compound an even larger hypsochromic

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[8] Szmant and Basso (manuscript in preparation), and previous investigators.

[9] Ferguson, *Chem. Revs.*, **43**, 428 (1948).

shift, and its position (230 mμ, ε 6,400) even suggests that this partial represents the resonance of only the thiophene ring.[10]

The secondary maximum of 2-(3-methylthienyl) styryl ketone differs from the 4- and 5-methyl analogs in the styryl ketones as much as it does in the methyl ketones, and presumably the hyperconjugation phenomenon suggested for the methyl ketone again is involved.

It is of interest to compare the spectrum of furfural-2-acetothienone with those of benzal-2-acetothienone (2-thienyl styryl ketone) and furfuralacetophenone.[8] The electron donating quality of the 2-furyl group is apparent from the bathochromic shift of the 310 mμ band of chalcone to 344 mμ (ε 26,800) in furfuralacetophenone. This shift of some 34 mμ is almost duplicated when the 2-furyl group replaces the phenyl group of benzal-2-acetothienone to give furfural-2-acetothienone (from 320 to 353 mμ). Similarly, the effect of the replacement of the phenyl by a 2-thienyl group gives an almost constant bathochromic shift of 9–10 mμ in both the furan and benzene series. Thus, the replacement of the phenyl group in chalcone by the 2-thienyl group causes a shift of the maximum from 310 mμ to 320 mμ, while the maximum of furfural acetophenone (344 mμ) is displaced in furfural-2-acetothienone to 353 mμ. The spectrum of furfural-2-acetothienone also exhibits the secondary maximum at 244 mμ typical of the secondary maxima encountered in the 2-thienyl styryl ketones.

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(10) The maxima of thiophene and alkyl thiophenes are reported in the 231–237 mμ range (Appleby, *et al.*, THIS JOURNAL, **70**, 1552 (1948); Kuhn and Dann, *Ann.*, **547**, 293 (1941); also ref. (5)).

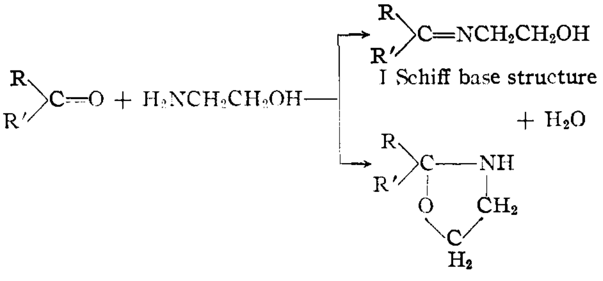
[CONTRIBUTION OF THE NAVAL RESEARCH LABORATORY]

Infrared Spectra and Structure of Reaction Products of Ketones and Ethanolamine[1]

BY L. W. DAASCH

The structure of products obtained in the condensation of aliphatic ketones with ethanolamine can be postulated to be either a Schiff base or an oxazolidine ring. The infrared spectra presented for some of these products indicates the Schiff base structure forms in preference to the oxazolidine ring structure. In certain instances this is contradictory to the structures reported on the basis of other physical properties.

The infrared spectra of the reaction products of certain aromatic aldehydes and ethanolamine have indicated that the structure in these cases was a Schiff base[2] rather than an oxazolidine.[3] It was of interest to extend the investigation to products prepared from aliphatic ketones and ethanolamine where the reaction could also lead either to a Schiff base (I) or an oxazolidine ring structure (II). The choice between these structures has previously been made on the basis of the compound's viscosity, refractive index, solubility in water, and on the difference in boiling points of the compound and its reduction product. By correlating these physical properties some of the compounds investigated here have been given structure (I) and others structure (II).[4] The structure of four ketone-ethanolamine condensation products has been determined through a study of their infrared spectra.



II Oxazolidine structure

Discussion

The infrared spectrum of compounds with structure (I) may be expected to show absorption around 1650 cm.$^{-1}$ due to the C=N bond while structure (II) should have no corresponding absorption.[2] Both structures should produce absorption bands around 3300 and 1150 cm.$^{-1}$ due to OH (bonded) and C–OH linkages, respectively, in structure (I), and due to NH (bonded) and C–O–C, respectively, in structure (II).[5] By obtaining the spectrum of dilute solutions in non-polar solvents one can frequently determine whether the 3300 cm.$^{-1}$ band is an OH or NH absorption and this provides another spectral difference between structures (I) and (II). In the present instance solution work was unnecessary since the C=N correlation reliably distinguishes between structures (I) and (II).

The spectra of compounds prepared from the reactions of methyl *n*-propyl ketone, diisobutyl ketone, methyl *n*-amyl ketone, and cyclohexanone with ethanolamine are shown in Figs. 1, 2, 3 and 5. Figures 4 and 6 are, respectively, the spectra of the compounds prepared from methyl *n*-amyl ketone and cyclohexanone with the secondary amine,

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(1) The opinions contained herein are the author's and are not to be construed as official or reflecting the views of the Department of Navy. Article not copyrighted.

(2) L. W. Daasch and U. E. Hanninen, THIS JOURNAL, **72**, 3673 (1950).

(3) L. H. Goodson and H. Christopher, *ibid.*, **71**, 1117 (1949).

(4) A. C. Cope and E. M. Hancock, *ibid.*, **64**, 1503 (1942).

(5) (a) R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948); (b) H. W. Thompson, *J. Chem. Soc.*, 328 (1948).