[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

Absorption Spectra. V. The Ultraviolet and Visible Spectra of Certain Polyene Aldehydes and Polyene Azines[1]

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In this paper we should like to report the results of some studies on the ultraviolet and visible absorption spectra of certain compounds containing conjugated double bonds. The substances studied were aldehydes of the generic formula, I

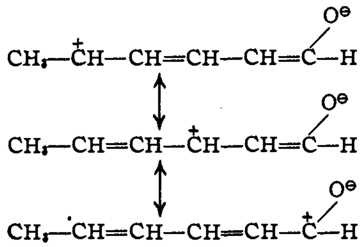
$$\mathrm{R{-}(CH{=}CH)_{\mathit{n}}{-}CHO} \qquad \mathrm{I}$$

where R is methyl or α-furyl and n ranges up to 7, and azines of the generic formula, II

$$\mathrm{R{-}(CH{=}CH)_{\mathit{n}}{-}CH{=}N{-}N{=}CH{-}(CH{=}CH)_{\mathit{n}}{-}R} \qquad \mathrm{II}$$

where R is methyl or α-furyl. Previous workers, notably Kuhn and his school, have prepared many compounds of the polyene type and have reported their absorption spectra. Their results on aldehydes of the Type I,[2,3] which did not extend beyond $n = 3$, are in essential agreement with our measurements.

The absorption spectra of the homologous series of aliphatic polyene aldehydes containing as many as seven conjugated carbon–carbon double bonds are shown in Figs. 1 and 2. The spectra of these compounds are characterized by a single intense absorption band which, in the higher members of the series, is accompanied by a weaker band at shorter wave lengths. As the length of the conjugated system is increased, both bands move toward longer wave lengths, but show no evidence of fine structure typical of the polyene hydrocarbons.[4] The intense band may probably be correlated with electronic transitions to relatively highly ionic states in which forms such as III (shown for 2,4-hexadienal) are prominent contributors. It is noteworthy that in the polyene aldehyde series the principal band lies at considerably longer wave lengths than the principal band of the aliphatic polyene hydrocarbon with the same number of carbon atoms. The carbonyl group produces a bathochromic effect by lengthening the conjugated system, increasing the number of resonance forms and thereby reducing the energy necessary to effect transitions from the ground state to the first excited state.[5]



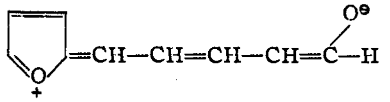
$$\begin{array}{c} \mathrm{CH_3{-}\overset{+}{C}H{-}CH{=}CH{-}CH{=}\overset{O^{\ominus}}{C}{-}H} \\ \updownarrow \\ \mathrm{CH_3{-}CH{=}CH{-}\overset{+}{C}H{-}CH{=}\overset{O^{\ominus}}{C}{-}H} \\ \updownarrow \\ \mathrm{CH_3{-}CH{=}CH{-}CH{=}CH{-}\overset{+}{C}(O^{\ominus}){-}H} \end{array} \qquad \mathrm{III}$$

TABLE I

Compound	Total no. of double bonds	λ max. in mμ	Spectral solvent
2,4-Hexadiene	2	227[a]	Hexane
Crotonaldehyde	2	212[b]	Hexane
2,4,6-Octatriene	3	263[c]	Hexane
		263[c]	Ethanol
2,4-Hexadienal	3	263[b]	Hexane
		271[c]	Ethanol
2,4,6,8-Decatetraene	4	295[c,d]	Hexane
2,4,6-Octatrienal	4	306[b]	Hexane
2,4,6,8,10,12-Tetradecahexaene	6	358[c,e]	Chloroform
2,4,6,8,10-Dodecapentaenal	6	380[c]	Chloroform

[a] Booker, Evans and Gillam, *J. Chem. Soc.*, 1453 (1940). [b] See ref. 2. [c] Present work. [d] Kuhn and Grundmann, *Ber.*, 71, 442 (1938), report maxima at 272, 284, 296 and 320 mμ. We find maxima at 272, 283, 295 and 310 mμ with the 295 maximum the most intense. [e] See also Kuhn, *Angew. Chem.*, 50, 703 (1937).

The spectra of the α-furyl polyene aldehydes (shown in Figs. 3 and 4) exhibit the same general characteristics as those of the aliphatic polyene aldehydes. In the furyl series the second less intense absorption band first appears in the trienal. In line with an earlier observation on the lower members of the series[3] we find that the higher furyl polyene aldehydes absorb at approximately the same wave lengths as the aliphatic polyene aldehydes containing the same total number of double bonds (Table II). Although the linear extension of the conjugated system in the furyl aldehydes is decreased by the presence of two of the double bonds in a ring, the increased contribution of dipolar forms such as IV (shown for 5-α-furyl-



IV

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[1] For the last paper in this series see Blout, Eager and Gofstein, THIS JOURNAL, **68**, 1983 (1946).

[2] Hausser, Kuhn, Smakula and Hoffer, *Z. physik. Chem.*, **29B**, 371 (1935).

[3] Hausser, Kuhn, Smakula and Deutsch, *ibid.*, **29B**, 378 (1935).

[4] Kuhn and Grundmann, *Ber.*, **71B**, 442 (1938).

[5] It is also possible that a group such as the carbonyl has an additional effect on the absorption due to its polar character. Since less energy is necessary to effect charge separation in a system containing a polar group, it is reasonable to assume that such a system will absorb light of longer wave lengths than a system containing an equal number of conjugated double bonds and no polar group. Comparison of the spectra of the aliphatic polyene aldehydes with the spectra of the aliphatic polyene hydrocarbons offers difficulty because of the fine structure shown by the latter compounds. If, however, one compares the *wave lengths of maximum absorption* of the aldehydes with those of the hydrocarbons this difficulty is obviated. These data are summarized in Table I. Except for the lowest members of the series, the data are in line with these considerations.

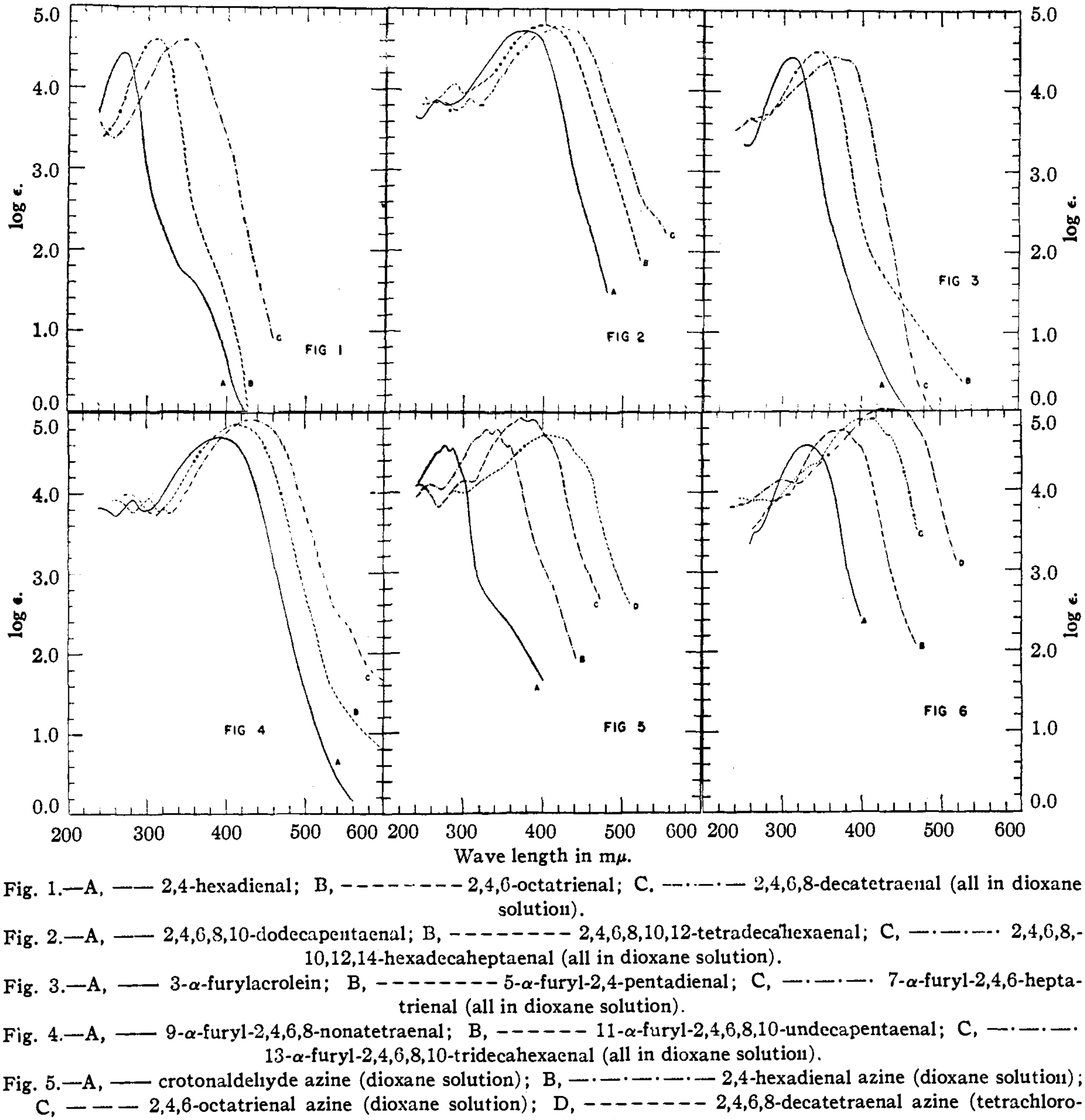

Fig. 1.—A, —— 2,4-hexadienal; B, -------- 2,4,6-octatrienal; C, —·—·— 2,4,6,8-decatetraenal (all in dioxane solution).

Fig. 2.—A, —— 2,4,6,8,10-dodecapentaenal; B, -------- 2,4,6,8,10,12-tetradecahexaenal; C, —·—·— 2,4,6,8,-10,12,14-hexadecaheptaenal (all in dioxane solution).

Fig. 3.—A, —— 3-α-furylacrolein; B, -------- 5-α-furyl-2,4-pentadienal; C, —·—·— 7-α-furyl-2,4,6-heptatrienal (all in dioxane solution).

Fig. 4.—A, —— 9-α-furyl-2,4,6,8-nonatetraenal; B, ------ 11-α-furyl-2,4,6,8,10-undecapentaenal; C, —·—·— 13-α-furyl-2,4,6,8,10-tridecahexaenal (all in dioxane solution).

Fig. 5.—A, —— crotonaldehyde azine (dioxane solution); B, —·—·—·— 2,4-hexadienal azine (dioxane solution); C, — — — 2,4,6-octatrienal azine (dioxane solution); D, -------- 2,4,6,8-decatetraenal azine (tetrachloroethylene solution).

Fig. 6.—A, —— furfural azine; B, — — — — 3-α-furylacrolein azine; C, --------- 5-α-furyl-2,4-pentadienal azine; D, —·—·— 7-α-furyl-2,4,6-heptatrienal azine (all in dioxane solution).

2,4-pentadienal) probably is sufficient to allow absorption at approximately the same wave length as the corresponding non-cyclic compound with the same number of double bonds. The increased contribution of forms such as IV may in turn be correlated with the ready acceptance of a positive charge by the ring oxygen atom.

In Fig. 7 we have plotted the wave lengths of the absorption maxima of the aliphatic and α-furyl polyene aldehydes as a function of the number of carbon–carbon double bonds. The plot for the main absorption bands, although definitely not a straight-line function with the lower members of the series, shows some evidence of linearity for several of the higher homologs. The position of the shorter wave length maximum appears to be a linear function of the number of double bonds for those members of the series examined. We have calculated the ratio of the wave length of maximum absorption of the longer wave length band to that of the shorter wave length band,[6] and find that in both series it decreases with increasing *n*. In this respect the absorption bands of the polyene aldehyde series differ from those of the

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(6) *Cf.* the second order bands described by Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

TABLE II

Compound	Color	Observed m. p., °C. (cor.)	Crystn. solvent	λ max. in mμ	log ε	λ max. in mμ	log ε	λ max. in mμ	log ε
Crotonaldehyde	Colorless	(B. p. 102.4)[a]		220[l]	4.17	322[l]	1.45		
2,4-Hexadienal	Colorless	(B. p. 63–63.5(15))[b]		271[l]	4.39	270[m]	4.43		
2,4,6-Octatrienal	Faint yellow	55.5–57.0[b]	Hexane	315[l]	4.57	312[m]	4.60		
2,4,6,8-Decatetraenal	Yellow	105.5–107[c]	Hexane	240[l]	3.52	351[l]	4.34	343[m]	4.60
				353[l]	4.61				
2,4,6,8,10-Dodecapentaenal	Golden yellow	166–167[d]	Ethanol	263[l]	3.97	377[l]	4.71		
				264[m]	3.76	370[m]	4.76	380[n]	4.76
				268[o]	3.93	380[o]	4.86		
2,4,6,8,10,12-Tetradecahexaenal	Red-orange	195–196[e]	Chloroform	285[m]	4.05	393[m]	4.81	399[n]	4.71
2,4,6,8,10,12,14-Hexadecaheptaenal	Deep red	219–220[e] (dec.)	Chloroform	305[m]	3.89	415[m]	4.80		
				310[n]	4.03	424[n]	4.85		
Crotonaldehyde azine	Light yellow	96–97[f]	Hexane	275[l]	4.59	283[l]	4.56		
				267[m]	4.51	275[m]	4.60	285[m]	4.55
2,4-Hexadienal azine	Yellow	175–176[g]	Methanol	~259[m,q]	4.10	327[m]	4.80	342[m]	4.80
				358[m]	4.57				
2,4,6-Octatrienal azine	Yellow-orange	232–233[g]	Dioxane	245[m]	4.10	304[m]	4.14	372[m]	4.94
				~389[m,q]	4.92				
2,4,6,8-Decatetraenal azine	Red-orange	dec. >250		343[p]	3.63	410[p]	4.20	438[p]	4.17
				~450[p,q]	3.93				
Furfural	Colorless	60.8(20)[h]		270[m]	4.17	313[m]	1.78		
3-α-Furylacrolein	Colorless	50.5–51.0[i]		312[m]	4.42				
5-α-Furyl-2,4-pentadienal	Light yellow	65–67[i]		346[m]	4.47				
7-α-Furyl-2,4,6-heptatrienal	Yellow	111–112[j]	Ether–ligroin	260[m]	3.72	366[m]	4.43	(382)[m]	(4.39)
9-α-Furyl-2,4,6,8-nonatetraenal	Orange	151–152[j]	Ethanol	282[m]	3.91	389[m]	4.69		
11-α-Furyl-2,4,6,8,10-undecapentaenal	Red	195–196[j]	Chloroform	260[m]	3.90	300[m]	3.91	412[m]	4.86
13-α-Furyl-2,4,6,8,10,12-tridecahexaenal	Deep red	219–219.5[j]	Chloroform	280[m]	3.98	320[m]	3.80	429[m]	4.92
Furfural azine	Light yellow	110–111.5[k]	Ethanol	334[m]	4.58				
3-α-Furylacrolein azine	Yellow	164–165[i]	Ethanol	364[m]	4.76	378[m]	4.78		
5-α-Furyl-2,4-pentadienal azine	Golden yellow	204–205[i]	Ethanol	398[m]	4.90	413[m]	4.90		
7-α-Furyl-2,4,6-heptatrienal azine	Reddish-bronze	241.5–242.5 (dec.)	Dioxane	300[m]	4.15	430[m]	5.04	444[m]	5.04

[a] Young, THIS JOURNAL, 54, 2498 (1932). [b] Ref. 11. [c] Ref. 9. [d] Ref. 12. [e] Ref. 10. [f] Ref. 15. [g] Kuhn and Hoffer, *Ber.*, 68, 2164 (1930). [h] Mains, *Chem. Met. Eng.*, 26, 779 (1919). [i] Ref. 15. [j] Ref. 14. [k] Minunni, *Gazz. chim. ital.*, 29, II, 467 (1899). Absorption spectra solvents: [l] ethanol, [m] dioxane, [n] anisole, [o] chloroform, [p] tetrachloroethylene. [q] ~denotes an inflection point.

carotenoid and diphenyl polyene series where the ratio of the wave length of maximum absorption of the longest wave length band to that of a shorter wave length band increases with the length of the chain and approaches 2.

As suggested by Lewis and Calvin[6] for the diphenyl polyenes, we have also plotted the square of wave length of maximum absorption *versus* the number of double bonds for both of the polyene aldehyde series. Other investigators[7] have noted that in these cases the lowest members of the series show a linear relation between λ^2 and n. Calculated from our data, the points for the four higher homologs of each type also fall on straight lines, albeit different ones from those of the lower members.

The spectra of the aliphatic polyene azines, II, where n = 1, 2, 3 and 4 are shown in Fig. 5. Besides the expected bathochromic shift with increasing chain length, one observes some evidence of band splitting of the type seen in the aliphatic polyene hydrocarbons. Experimental difficulties, due to the insolubility of these compounds, have thus far limited our studies to the lower members of the series. The maximal absorptions of the aliphatic polyene azines lie at much shorter wave lengths than those of the aliphatic polyene hydrocarbons with the same number of double bonds (*cf.* Tables I and II). Since one might expect that systems containing the same number of conjugated double bonds and no highly polar groups would absorb at approximately the same positions, the absorption of the azines at much shorter wave lengths than their hydrocarbon analogs must mean that the effective absorbing system is shorter in

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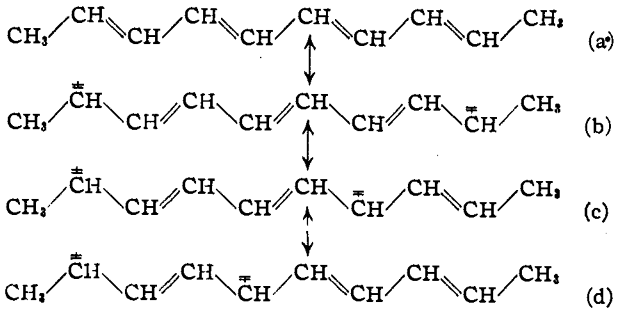
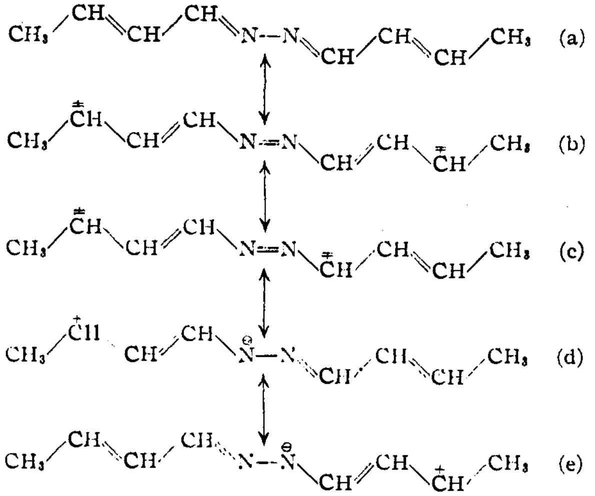
(7) Ferguson and Branch, THIS JOURNAL, 66, 1467 (1944).

the nitrogen-containing compounds. Some of the possible resonance forms of a polyene hydrocarbon are shown in V



V

and of the azine with the same number of double bonds in VI.



VI

The presence of the relatively electronegative nitrogen atoms in the azines leads to an increased contribution of forms such as VId and e to the resonance hybrid VI as compared with the contribution of forms such as Vd to the resonance hybrid V, and this favors absorption at shorter wave lengths.

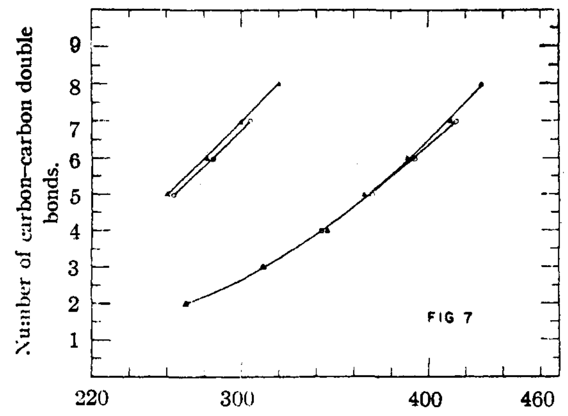


Fig. 7.—Wave lengths of maximum absorption *vs.* number of carbon–carbon double bonds in polyene aldehydes: ⊙—⊙, aliphatic polyene aldehydes; △—△, furyl polyene aldehydes.

The four lowest α-furyl polyene azines have similar absorption spectra (Fig. 6). Comparison of these spectra with those of the aliphatic polyene azines with the same number of double bonds (Fig. 5) shows that the maximal absorptions in the furyl series lie at shorter wave lengths than in the aliphatic series. This is consistent with the generalizations developed above inasmuch as in the furyl series forms containing negatively charged nitrogen atoms should be even larger contributors to the excited state because of the ready acceptance of the positive charge by the oxygen in the furan ring.

The absorption spectra of ω,ω'-diphenyl polyene azines containing as many as six double bonds in the linear portion of the molecule have already been measured by previous workers.[7] On comparing these data with the results of Kuhn's measurements[8] on some of the corresponding diphenylpolyene hydrocarbons, we note that in all cases the azines absorb at shorter wave lengths than the analogous hydrocarbons.

It has already been pointed out by Lewis and Calvin[5] that polyene azines should absorb at shorter wave lengths than the corresponding polyene hydrocarbons because of the greater "strain" of forms (such as VIb and c) which contain the —N═N— group. Our concept of this effect emphasizes the relatively greater contribution of forms containing charged nitrogen atoms as compared with forms in which the nitrogen atoms bear no formal charge. It appears to us that in this fact lies the reason for the differences in the ultraviolet absorption spectra of the polyene azines and the polyene hydrocarbons.

Acknowledgment.—We wish to acknowledge the assistance of Messrs. Marshall Kane and Claude Valle, who prepared many of the compounds, and Miss Adelaide Sutton, who measured the absorption spectra.

Experimental

Aliphatic Polyene Aldehydes.—These aldehydes were all prepared by modifications of the procedures of Kuhn and co-workers who condensed crotonaldehyde with itself or with acetaldehyde in the presence of piperidine acetate. Although the aliphatic polyene aldehydes undergo more or less rapid decomposition under ordinary conditions, they can be stored in vacuum at −50° for several months without change.

Condensation of Crotonaldehyde with Acetaldehyde.[9]—A solution of 380 cc. of acetaldehyde and 280 cc. of crotonaldehyde (Niacet, redistilled, b. p. 100–102°) in a 1-liter flask equipped with a Dry Ice condenser and a gas inlet tube was deaerated with nitrogen for thirty minutes; this precaution appears to be required in these reactions in

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[8] Hausser, Kuhn and Smakula, *Z. phys. Chem.*, **29B**, 384 (1935).

[9] Kuhn, Badstübner and Grundmann, *Ber.*, **69**, 98 (1936).

order to approximate the yields of condensation products reported by Kuhn and co-workers. After addition of 4 cc. of piperidine and 2.8 cc. of acetic acid, the reaction mixture was allowed to stand under nitrogen for eighteen hours. The clear red solution obtained after extracting the mixture with 1 liter of ether was filtered, washed well with water, dried over anhydrous sodium sulfate and stored at 0° for forty-eight hours. The small quantity of the red 2,4,6,8,10,12-tetradecahexaenal which had separated was filtered, washed with ether, and crystallized from chloroform. The yield of the pure hexaenal, m. p. 194–195°,[10] was 0.29 g.

Distillation of the ether filtrate in vacuum afforded, in three fractions, crude 2,4-hexadienal, 2,4,6-octatrienal and 2,4,6,8-decatetraenal in approximately the quantities reported by Kuhn, Badstübner and Grundmann.[9]

Distillation of the crude dienal fraction through an efficient column afforded 18.1 g. of 2,4-hexadienal, b. p. 62–65° (14 mm.). The sample used for absorption spectra measurements was distilled, retaining the middle fraction, b. p. 63.0–63.5° (15 mm.) (n^{20}D 1.5298), reported 64–66° (11 mm.),[1] n^{22}D 1.5372.

Isolation of pure 2,4,6-octatrienal was most effectively accomplished by cooling the crude fraction in a Dry Ice–butyl cellosolve bath, filtering the crystalline product, and then distilling the residual oil. The distillation of this oil yielded a fraction boiling at 74–85° (1.5 mm.) which afforded a considerable quantity of crystalline trienal upon cooling in a Dry Ice-bath. The crystallization of the total amount of crude cystalline material from its own weight of hexane gave 7.2 g. of octatrienal, m. p. 57–59°. After two more crystallizations from hexane the aldehyde melted at 55.5–57°; reported, 55°.[11]

Distillation of the crude decatetraenal fraction in a manner similar to that described above yielded 0.7 g. of the pure aldehyde, which melted at 105.5–107°, in good agreement with the value reported by Kuhn and co-workers.[9]

Self-Condensation of Crotonaldehyde.—This reaction was performed with deaerated crotonaldehyde essentially as described by Kuhn and Grundmann.[12,13] Although the yields of crude 2,4,6-octatrienal, 2,4,6,8,10-dodecapentaenal, and 2,4,6,8,10,12,14-hexadecaheptaenal were approximately those obtained by the previous workers, the yields of the pure compounds were considerably lower.

Furylpolyene Aldehydes.—Syntheses of these aldehydes were also achieved by condensation reactions as described in the literature.[14,15] The properties of our samples of these compounds, summarized in Table II, correspond with those reported.

Polyene Azines.—Most of the azines studied were known compounds whose preparation was accomplished by refluxing for several hours an ethanol or dioxane solution of 2.1 moles of aldehyde with 1 mole of 85% hydrazine hydrate.

Because of difficulties encountered with the method of Hladík,[16] an improved procedure for the preparation of crotonaldehyde azine had to be developed. One hundred and twenty-six cubic centimeters of 85% hydrazine hydrate was added dropwise at 0° to 300 g. of vigorously stirred crotonaldehyde; extraction of the reaction mixture with hexane yielded a clear yellow extract. Stored overnight at −50°, the washed and dried hexane solution deposited 15 g. of crude crotonaldehyde azine, m. p. 63–94°. After several crystallizations from hexane 5.3 g. of material, m. p. 98–101°, was obtained. Although several more crystallizations failed to sharpen the melting point, the pure azine, m. p. 101.5–102°, was finally obtained with small loss by sublimation followed by one more crystallization from hexane. Crotonaldehyde azine is reported by Hladík to melt at 96°.

2,4,6,8-Decatetraenal Azine.—A satisfactory analytical sample of this azine could not be prepared. The extremely slight solubility of the substance rendered crystallization impracticable and high vacuum sublimation (10^{-4} mm.) was accompanied by considerable decomposition. The compound decomposed without melting at about 250°.

Anal. Calcd. for $C_{20}H_{24}N_2$: C, 82.14; H, 8.27. Found: C, 82.03; H, 8.87.

7-α-Furylheptatrienal Azine.—This substance crystallizes from dioxane in tiny bronze colored needles, m. p 241.5–242.5° dec.

Anal. Calcd. for $C_{22}H_{20}O_2N_2$: C, 76.75; H, 5.86. Found: C, 76.47; H, 6.30.

Spectral Measurements.—The absorption spectra measurements were made on a Beckman Quartz Spectrophotometer Model DU using a 1-cm. quartz cell and a hydrogen discharge tube as an ultraviolet source. Because of the wide variation in the solubilities of the substances investigated it was impossible to make all measurements in a single solvent. When, because of the lower solubility of the higher members of a homologous series it was necessary to change the solvent for spectral measurements, we obtained data for intermediate members in both solvents. Although the magnitude of the shift of the absorption maxima due to changes in solvent was not constant, it was always in the direction of shorter wave lengths when one changed from anisole or ethanol to dioxane (Table II).

Ethanol.—Commercial absolute ethanol was used without purification.

1,4-Dioxane.—The material used in the early phase of the work was purified by the standard method[17]; but when it was found that a commercial product[18] was satisfactory after refluxing for three days over sodium followed by distillation, the abbreviated treatment was adopted. Stored over sodium wire with minimum contact with air, the pure solvent, b. p. 100.5–101.0°, was suitable for spectrophotometric measurements at wave lengths as short as 238 mμ.

Anisole.—Distillation of Eastman Kodak Co. "White Label" grade gave a product, b. p. 152–153°, satisfactory for spectrophotometric measurements at wave lengths greater than 295 mμ.

Tetrachloroethylene.—The commercial product was distilled, retaining the middle fraction, b. p. 120–121°.

Summary

The ultraviolet and visible absorption spectra of certain polyene aldehydes of the type R—(CH═CH)$_n$—CHO, where R is methyl or α-furyl, have been determined. The spectra of azines prepared from the lower members of both polyene aldehydes series have been measured. Correlation of these data with those of other polyenic compounds has been attempted.

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(10) Schmitt and Obermeit, *Ann.*, **547**, 285 (1941).

(11) Kuhn and Hoffer, *Ber.*, **64**, 1977 (1931); Baumgarten and Glatzel, *ibid.*, **59**, 2662 (1926).

(12) Kuhn and Grundmann, *ibid.*, **70**, 1318 (1937).

(13) Kuhn, *Angew. Chem.*, **50**, 706 (1937).

(14) Schmitt, *Ann.*, **547**, 282 (1941).

(15) Hinz, Meyer and Schucking, *Ber.*, **76B**, 676 (1943).

(16) Hladík, *Monatsh.*, **24**, 440 (1903).

(17) Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., Boston, Mass., 1941, p. 368.

(18) Union Carbide and Carbon Corporation.