1.0 g. (95%) of V crystallized (the yield using IV was 43%); recrystallized from 60–90° ligroin, m.p. 93°.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.99; H, 6.71. Found: C, 87.89; H, 6.58; λ_{max} 260 mμ, ϵ 15,500; $\lambda_{min.}$ 242 mμ, ϵ 11,100; breadth of band at ϵ 12,000, 243–282 mμ; no infrared bands at 2.8–3.0 μ or at 5.8–6.1 μ.

α,β-Diphenylchalcone (VIII)[10]: m.p. 153°. *Anal.* Calcd. for $C_{27}H_2O$: C, 89.97; H, 5.59. Found: C, 89.74; H, 5.50; λ_{max} 242 mμ, ϵ 25,000; shoulder at 285 mμ, ϵ 12,000.

1-Ethoxy-1,2,3-triphenylindene[17] was obtained as a by-product in one preparation of α,β-diphenylchalcone (VIII) where technical (non-dried) bromine was used and the ether solution was dried, evaporated and treated with ethanol; m.p. 171–172° (K[17], 172°). It was characterized by analysis and absorption spectra; λ_{max} 245, 322 mμ, ϵ 25,200, 10,500; λ_{min} 277 mμ, ϵ 3,500; no infrared absorption bands at 2.8–3.0 or 5.8–6.1 μ.

1,2,3,3-Tetraphenyl-2-propene-1-ol (IX).—A slurry of 2 g. of the ketone VIII in 175 ml. of ether was added to 1 g. of lithium aluminum hydride in 50 ml. of ether with continued stirring for 20 min.; crystallized from 60–90° ligroin; 2.0 g. (99%), m.p. 93–103°. Slow recrystallization gave large colorless needles of similar wide melting range.

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.31; H, 6.03. Found: C, 89.28; H, 6.22; ultraviolet absorption, decreasing from 220–340 mμ with pronounced shoulder at 270 mμ, ϵ 9,600.

Dehydration of *cis*-1,1,2,3-tetraphenyl-2-propen-1-ol (a *trans*-cinnamyl alcohol) (XI) by refluxing 88% formic acid (1 hr.) gave 1,2,3-triphenylindene in 99% yield (identified by mixture m.p. with an authentic sample[17]).

Dehydration of 1,2,3,3-tetraphenyl-2-propen-1-ol (IX) similarly gave 67% of 1,2,3-triphenylindene (identified).

1,2,3-Triphenylindene[17,18]: m.p. 133–134°. *Anal.* Calcd. for $C_{22}H_{20}$: C, 94.17; H, 5.85. Found: C, 93.70; H, 5.79.

Reaction of phenyllithium with α,β-diphenylchalcone (VIII), carried out exactly according to the above procedure for II, gave 67% yield of 1,1,2,3,3-pentaphenyl-2-propene-1-ol (XII)[10]; crystallized from chloroform–ligroin mixture, m.p. 164–169° (identified by m.p. analysis and spectral data, and the m.p. 217–218° of its acetate[10]).

Anal. Calcd. for $C_{33}H_{26}O$: C, 90.38; H, 5.98. Found: C, 90.00; H, 5.89; λ_{max} 265–280 mμ, ϵ 7,500; $\lambda_{min.}$ 255 mμ, ϵ 6,200; infrared band at 2.86 μ; none at 5.8–6.1 μ.

CHARLOTTESVILLE, VIRGINIA

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[17] E. P. Kohler, *Am. Chem. J.*, **40**, 222 (1910).

[18] E. P. Kohler and W. E. Mydans, THIS JOURNAL, **54**, 4667 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

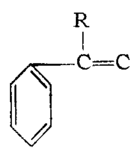
Ionic Polymerization.[1] A Convenient Synthesis of α- and β-Alkylstyrenes. The Effect of an α-Alkyl Group on the Ultraviolet Absorption Spectra

BY C. G. OVERBERGER AND DAVID TANNER[2]

RECEIVED MAY 28, 1954

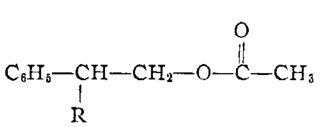
A convenient synthesis of α- and β-alkylstyrenes by the deacetylation of the acetates from carbinols II and III is reported. Evidence is presented for the structure of the styrenes based on ozonolysis and correlation of fractional distillation data and ultraviolet absorption spectra. Steric inhibition of resonance in the case of α-alkylstyrenes is suggested based on the interpretation of the ultraviolet absorption spectra.

In order to determine quantitatively the steric effect of alkyl groups on the rate of addition of an ion pair to a vinyl group by use of the copolymerization technique, a series of pure α- and β-alkylstyrenes have been prepared. This paper reports the preparation and characterization of I, R = C_2H_5, R′ = H; R = n-C_3H_7, R′ = H; R = iso-C_3H_7, R = H; R = H, R′ = CH_3; R = H, R′ = C_2H_5 and R = H,R′ = n-C_3H_7. Copolymerization data will be reported separately.


I

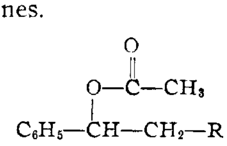
Although these styrenes have previously been prepared in a variety of ways, we wish to report a convenient preparation for the pure monomers by deacetylation of II to obtain the α-alkylstyrenes and III to obtain the β-alkylstyrenes. Furthermore, the preparation of the pure monomers by one investigator has made it possible to compare their physical properties.

Examination of the literature revealed that dehydration[3] or dehydrohalogenation[4] of the appropriate alcohol or alkyl halide, respectively, for the preparation of α-alkylstyrenes usually gave mixtures of products, either due to double bond isomerization or rearrangement of the carbon skeleton. Reported decarboxylations of β-alkylcinnamic acids were unsatisfactory for large scale preparation due to small yields.[5] Since deacetylation is known to proceed through a cyclic mechanism without rearrangement,[6] this method seemed preferable for the preparation of pure α-alkylstyrenes.



$$C_6H_5-\underset{R}{\underset{|}{CH}}-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3$$

II



$$C_6H_5-\overset{O-\overset{O}{\overset{\|}{C}}-CH_3}{\overset{|}{CH}}-CH_2-R$$

III

The synthesis of the β-alkylstyrenes was effected by a similar procedure, although many other useful procedures are recorded in the literature (Table III).

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[1] This is the fourth in a series of papers concerned with ionic catalyzed polymerization; for the third, see C. G. Overberger, R. J. Ehrig and D. Tanner, THIS JOURNAL, **76**, 772 (1954).

[2] A portion of a thesis submitted by D. Tanner in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] (a) Footnote *a*, ref. 1, Table III; (b) Mme. Ramart-Lucas and Mlle. Amagat, *Compt. rend.*, **184**, 30 (1927); (c) P. Ramart and P. Amagat, *Ann. chim.*, **8**, 263 (1927); (d) Mme. Ramart-Lucas and P. Amagat, *Bull. soc. chim.*, **15**, 108 (1932).

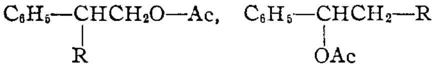
[4] (a) Footnote *c*, ref. 1, Table III; (b) C. R. Hauser, P. S. Skell, R. D. Bright and W. B. Renfrow, THIS JOURNAL, **69**, 589 (1947).

[5] Footnote *a*, ref. 2, Table III; footnote *b*, ref. 1, Table III.

[6] E. R. Alexander and A. Mudrak, THIS JOURNAL, **72**, 1810 (1950); see also reference 18 for discussion and earlier references.

TABLE I

SUBSTITUTED PHENYLETHYL ACETATES



$C_6H_5—\underset{R}{CH}CH_2O—Ac$, $C_6H_5—\underset{OAc}{CH}CH_2—R$

R group	B.p., °C.	B.p., Mm.	$n^{25}D$	d^{25}_4	Yield,[e] %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
α-C_2H_5	91	2	1.4915	0.9932	82	$C_{12}H_{16}O_2$	74.96[f]	75.13	8.38	8.46
α-*n*-C_3H_7	112	4	1.4882	1.0082	80	$C_{13}H_{18}O_2$	75.69[f]	75.88	8.79	8.70
α-*i*-C_3H_7[a]	105	4	1.4903	0.9973	78	$C_{13}H_{18}O_2$	75.69[g]	75.41	8.79	8.71
β-CH_3[b]	82	4	1.4893	.9891	83	$C_{11}H_{14}O_2$	74.12[f]	74.23	8.19	8.36
β-C_2H_5[c]	92	4	1.4866	.9936	83	$C_{12}H_{16}O_2$	74.96[f]	74.77	8.38	8.26
β-*n*-C_3H_7[d]	96	2	1.4852	.9862	80	$C_{13}H_{18}O_2$	75.69[f]	75.69	8.79	8.89

[a] E. E. Blaise and A. Courtot, *Bull. soc. chim.*, [3] **35**, 595 (1906), reported b.p. 135° (15 mm.), prepared from the alcohol and acetic anhydride. [b] Errera, *Gazz. chim. ital.*, **16**, 323 (1886), b.p. 227–228°, from 1-phenyl-1-chloropropane and silver acetate; P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **97**, 379 (1932), b.p. 130° (35 mm.), d^{24}_4 1.006. [c] V. Grignard, *Ann. chim. phys.*, [7] **24**, 467 (1901), b.p. 117–118° (8 mm.); P. H. Levine and R. E. Marker, footnote *b*, b.p. 134° (30 mm.), d^{22}_4 1.0000; J. Kenyon and S. M. Partridge, *J. Chem. Soc.*, 128 (1936), b.p. 125° (16 mm.), $n^{20.5}D$ 1.4889, by heating the carbinol with acetic anhydride in pyridine. [d] P. A. Levene and R. E. Marker, b.p. 140° (20 mm.), d^{22}_4 0.988. [e] After fractionation. [f] Analysis by Schwartzkopf Microanalytical Laboratory, Elmhurst, N. Y. [g] Analysis by Dr. K. Ritter, Zurich, Switzerland.

TABLE II

PYROLYSIS OF PHENYLETHYL ACETATES

R Group	Drops/ sec.	Tube temp., °C.	Wt. of acetates, g.	Wt. of uncracked acetates, g.	Styrene, yield, %	$n^{25}D$
α-C_2H_5	1.3	492–506	35	3	76[a]	1.5283[a]
α-C_2H_5	1.0	486–526	34	3	71[a]	1.5270[a]
α-C_2H_5	1.0	540–562	25	0	79[a]	1.5272[a]
α-C_2H_5	1.0	517–560	130	18	67[b]	1.5264[b]
α-*n*-C_3H_7	1.0	520–550	82	0	60[b]	1.5195[b]
α-*i*-C_3H_7	0.7	550–560	101	0	60[b]	1.5146[b]
β-CH_3	1.5	516–572	55	0	81[a]	1.5454[a,c]
β-CH_3	1.0	539–588	46	0	85[a]	1.5449[a,c]
β-CH_3	0.7	520–550	206	0	83[a]	1.5461[a,c]
β-C_2H_5	0.7	420–468	26	5	59[a]	1.5356[a,d]
β-C_2H_5	1.0	540–660	70	0	60[a]	1.5425[a,d]
β-C_2H_5	1.0	530–566	100	0	72[a]	1.5367[a,d]
β-C_2H_5	1.0	508–520	100	0	74[a]	1.5359[a,d]
β-C_2H_5	1.0	510–554	195	0	70[a]	1.5346[a,d]
β-*n*-C_3H_7	1.0	526–554	140	0	50[b]	1.5455[b]

[a] After distillation but before fractionation. [b] After fractionation. [c] After fractionation, $n^{25}D$ 1.5487. [d] After fractionation, $n^{25}D$ 1.5401

For the preparation of the alcohols corresponding to II, the appropriate acids were reduced to the alcohols in high yield by means of lithium aluminum hydride.[7] The secondary alcohols similar to structure III were prepared by reduction of the appropriate ketone with the same reagent. With one exception (Experimental section) these alcohols (II and III) are known and described in the literature prepared by other methods. The yields for these reductions are high ($R = C_2H_5$, $R' = H$, 89%; $R = n\text{-}C_3H_7$, $R' = H$, 91%; $R = \text{iso-}C_3H_7$; $R' = H$, 80%; $R = H$, $R' = CH_3$, 87%; $R = H$, $R' = n\text{-}C_3H_7$, 83%) and this method is a preferred procedure. Complete experimental details and comparison of physical data with other reported values are omitted for brevity and can be obtained from the senior author on request. The acids used in the reduction for the α-alkyl sequence were prepared by hydrolysis of the corresponding nitriles. In one case (α-isopropyl) hydrolysis of α-phenylisovaleronitrile gave exclusively the amide under conditions in which α-phenyl-*n*-valeronitrile (α-*n*-propyl) gave only acid indicating a considerable steric effect. The amide was then reduced directly to the alcohol with sodium and ethanol.[4b] The properties of the acetates are described in Table I. Pyrolysis experiments are described in Table II and the styrenes are described in Table III. All of the styrenes we prepared were purified carefully by fractional distillation. For the α-alkylstyrenes, the fractionations indicated only one product and it therefore is very unlikely that isomerization of the double bond or rearrangement of the carbon skeleton had occurred. Further confirmation of the structure of the α-alkylstyrenes was afforded by ozonolysis. Formaldehyde and ethyl phenyl, propyl phenyl and isopropyl phenyl ketones were the only products found on ozonolysis of α-ethyl, α-*n*-propyl and α-isopropylstyrenes, respectively. Formaldehyde dimethone and the 2,4-dinitrophenylhydrazones of the above ketones were isolated in greater than 50% yields. Although this evidence does not exclude the possibility of small amounts of isomeric products, these degradative products along with the absence of any indication of other isomers from the fractionation data strongly indicate the proposed structures.

For the β-alkylstyrenes, careful fractional distillation gave a homogeneous product, but initial fractions indicated the presence of an isomeric material. There was a steady increase in refractive index from $n^{25}D$ 1.5402 to 1.5498 for β-methyl and 1.5380 to 1.5439 for β-ethylstyrene in the initial fractions. It appeared at first that pyrolysis had resulted in the isomerization of the double bond. This view was supported by ultraviolet absorption spectra of lower boiling fractions (Table V) which gave lower extinction coefficients. Any migration of the double bond out of conjugation with the ring would decrease absorption. However, reaction with potassium hydroxide at high temperatures of fractions having the lower intensity resulted in no change in the boiling point or refractive index of the starting materials indicating that the double bond already had been conjugated with the benzene ring. This suggested that the lower boiling product was a *cis* isomer and we will report on this problem in the future.

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(7) (a) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947); (b) R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 2548 (1947).

TABLE III

SIDE CHAIN ALKYL SUBSTITUTED STYRENES

R group	B.p., °C. (atm.)	n^{25}D	d^{25}_4	Formula	Percentage composition[f] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
α-C$_2$H$_5$[a]	181	1.5264	0.8868	$C_{10}H_{12}$				
α-n-C$_3$H$_7$[b]	201	1.5195	.9042	$C_{11}H_{14}$	90.35	90.50	9.65	9.59
α-i-C$_3$H$_7$[c]	192	1.5146	.8954	$C_{11}H_{14}$	90.35	90.30	9.65	9.64
β-CH$_3$[d]	176	1.5487	.9155	C_9H_{10}	91.46	91.27	8.56	8.57
β-C$_2$H$_5$[e]	200	1.5401	.9070	$C_{10}H_{12}$	90.84	90.90	9.15	9.16

[a] S. Sabetay, *Bull. soc. chim.*, [4] **47**, 614 (1930), reported b.p. 177–180° (742 mm.), n^{22}D 1.5262, prepared by the action of anhydrous potassium hydroxide on 2-phenylbutanol-1; J. D. A. Johnson and G. A. R. Kon, *J. Chem. Soc.*, 2748 (1926), b.p. 81–82° (20 mm.), 18%, by boiling β-ethylcinnamic acid with 50% sulfuric acid; oxidation with potassium permanganate gave propiophenone. [b] M. Tiffeneau, *Ann. chim. phys.*, [8] **10**, 322 (1907), b.p. 198–202°, d_0 0.9138, by decarboxylation of β-propylcinnamic acid dibromide; Johnson and Kon, footnote *a*, b.p. 86° (14 mm.), 33–47%, by boiling β-propylcinnamic acid with 50% sulfuric acid, oxidn. with potassium permanganate gave butyrophenone. [c] A. Klages, *Ber.*, **36**, 3688 (1903), b.p. 82° (12 mm.), 191–192° (753 mm.), $d^{13.8}_4$ 0.8991, n^{13}D 1.5181, by heating 1-chloro-1-phenyl-1,2-dimethylpropane with pyridine at 125°, oxidation with chromic acid yielded isobutyrophenone; Johnson and Kon, footnote *a*, b.p. 89° (15 mm.), 31–38%, by boiling β-isopropylcinnamic acid with 50% sulfuric acid, oxidation with potassium permanganate gave isobutyrophenone. [d] A. Klages, *Ber.*, **36**, 2572 (1903), b.p. 177° (756 mm.), d^{20}_4 0.9141, n^{20}D 1.5492, by warming 1-chloro-1-phenyl-2-bromopropene-1, with sodium and alcohol; A. Bruylants, *Bull. soc. chim. Belges*, **59**, 421 (1950), b.p. 64° (10 mm.), d^{15}_4 0.9158, n^{15}D 1.5524, by dehydration of the corresponding alkylphenylcarbinol with a trace of H_2SO_4, side reactions led to ketones and to cyclic trimers of the corresponding ketones; L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 2283 (1951), b.p. 65° (14 mm)., n^{19}D 1.5490, by isomerization of allylbenzene. [e] A. Klages, *Ber.*, **37**, 2312 (1904), b.p. 89–90° (15 mm.), d^{16}_4 0.9124, n^{16}D 1.5414, from 1-chloro-1-phenylbutane and pyridine at 125°, A. Bruylants, footnote *d*, b.p. 76° (10 mm.), d^{15}D 1.5467, by dehydration of the corresponding alkylphenylcarbinol with a trace of sulfuric acid, side reaction led to ketones and to cyclic trimers; R. Ya. Levina and N. A. Shcheglova, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 527 (1941), b.p. 65.5–66° (4 mm.), n^{20}D 1.5378, d^{20}_4 0.9006, obtained by isomerization of 4-phenyl-1-butene over Al_2O_3 at 250°, dibromide. [f] Analyses by Schwarzkopf Microanalytical Laboratory, Elmhurst, N. Y.

The marked difference in absorption between α-alkylstyrenes, styrene and β-alkylstyrenes (Table IV)[8] is of interest. The extinction coefficient of styrene is greatly reduced when an alkyl group is substituted in the α-position. The extinction coefficient maxima decreases progressively from 14,620 for styrene to 11,400, 10,100, 9,390 and 7,800 (hyperchromic shift) for α-CH$_3$, α-C$_2$H$_5$, α-n-C$_3$H$_7$ and α-iso-C$_3$H$_7$ styrene, respectively. There is also a small but significant hypsochromic effect. This indicates that steric inhibition of resonance may exist here and markedly effects the absorption spectra. The ultraviolet absorption spectra of β-methylstyrene and α-methylstyrene have been reported previously. Koch[9] has discussed the spectra of the β-methyl compound in detail.[3c] In the case of β-alkyl groups there are two effects operating. The extinction coefficient (ϵ) increases from 14,620 for styrene to 17,300 and 17,640 for β-CH$_3$ and β-C$_2$H$_5$, respectively, for the large absorption maxima ($\lambda_{max.}$ 2510 Å.) with corresponding increases in the second, 2840 Å., and third peaks, 2930 Å., as well. Here there is a small increase toward longer wave lengths. In addition to a steric effect there may be additional resonance contributions resulting from hyperconjugation.

A lower boiling fraction (n^{25}D 1.5446) of β-methylstyrene had an extinction coefficient maxima for three peaks of 16,200 ($\lambda_{max.}$ 2510), 750 ($\lambda_{max.}$ 2840) and 455 ($\lambda_{max.}$ 2930), while a higher boiling fraction (n^{25}D 1.5471) had 16,700, 970 and 620. A lower boiling fraction (n^{25}D 1.5372) of β-ethylstyrene had extinction coefficient maxima of 16,000, 1,030 and 640 while a higher boiling fraction (n^{25}D 1.5392) had 17,700, 1,190 and 755. If steric effects are the reason for this hypochromic effect then the higher boiling fraction may be the *trans* form and the small amount of lower boiling fraction, the *cis* form.

TABLE IV

ULTRAVIOLET ABSORPTION SPECTRA OF NUCLEAR AND SIDE CHAIN ALKYL STYRENES

Alkyl styrenes	Absorption peaks I λmax	I ϵmax	II λmax	II ϵmax	III λmax	III ϵmax	IV λmax	IV ϵmax
β-C$_2$H$_5$	251	17,640	..	..	284	1125	293	725
β-CH$_3$	251	17,300	..	..	284	956	293	621
Styrene	248	14,620	273	768	282	759	291	534
α-CH$_3$	243	11,400	..	..	..	..	..	..
α-C$_2$H$_5$	240	10,100	..	..	..	..	..	..
α-n-C$_3$H$_7$	239	9,390	..	..	..	..	..	..
α-i-C$_3$H$_7$	234	7,800	..	..	..	..	..	..

Experimental[10]

Preparation of Carbinols.—A typical example is illustrated. 2-Phenylbutanol-1 was prepared in 89% yield from 16.42 g. (0.1 mole) of α-phenylbutyric acid (Eastman Kodak Co.) and 4.75 g. (0.125 mole) of lithium aluminum hydride, b.p. 81° (2 mm.), n^{24}D 1.5178. In a typical experiment, the product was obtained sufficiently pure to use directly without distillation: b.p. 120–121° (15 mm.), prepared by reduction of the amide with sodium and alcohol[3b]; b.p. 120–121° (18 mm.), by reduction of the amide[3c]; b.p. 95–96° (4 mm.), by treating (2-phenylethyl)-ethyl amide with nitrous acid[11]; b.p. 122–123 (18 mm.), 75% by reduction of the amide.[4b]

α-Phenylvaleronitrile was prepared from benzyl cyanide by alkylation with sodium amide and n-propyl iodide according to the procedure described by Hancock and Cope[12] who prepared α-cyclohexylphenylacetonitrile. From 82 g. (0.70 mole) of benzyl cyanide and 128 g. (0.80 mole) of n-propyl iodide there was obtained 88 g. (70%) of α-phenylvaleronitrile, b.p. 96–98° (2 mm.), n^{24}D 1.5025 (b.p. 255–261°, no yield given[13]).

Anal.[14] Calcd. for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 83.01; H, 8.37; N, 8.78.

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(8) The spectra have been deposited as Document number 4330 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints or $1.25 for 35 mm. microfilm payable to: Chief, Photoduplication Service, Library of Congress.

(9) H. P. Koch, *J. Chem. Soc.*, 1123 (1948).

(10) All melting points are uncorrected.

(11) P. A. Levene, L. A. Mikeska and K. Passoth, *J. Biol. Chem.*, **88**, 27 (1930).

(12) E. M. Hancock and A. C. Cope, *Org. Syntheses*, **25**, 25 (1945).

(13) R. H. Pickard and J. Yates, *J. Chem. Soc.*, **95**, 1017 (1909).

(14) Analyses by Dr. K. Ritter, Zurich, Switzerland; Dr. F. Schwarzkopf, Elmhurst, N. Y.

TABLE V

ULTRAVIOLET ABSORPTION SPECTRA OF FRACTIONS OF β-METHYL AND β-ETHYLSTYRENE

				Absorption peaks					
				I		II		III	
Alkylstyrene	Fraction	n^{25}_D	Wt., g.	λmax (mμ)	εmax	λmax (mμ)	εmax	λmax (mμ)	εmax
β-CH_3	1	1.5446	22	246	16,200	283	750	292.5	455
β-CH_3	2	1.5456	22	247	16,200	283.5	934	292.5	600
β-CH_3	3	1.5471	10	248	16,700	283.5	970	292.5	620
β-C_2H_5	1	1.5372	10	248	16,000	283.5	1030	292.5	640
β-C_2H_5	2	1.5387	10	249	17,700	283.5	1200	292.5	760
β-C_2H_5	3	1.5392	3	250	17,700	283.5	1190	292.5	755

α-Phenylvaleric acid was prepared by hydrolysis of α-phenylvaleronitrile. The method of hydrolysis recommended by Rossalymo[15] is to heat the nitrile with hydrochloric acid at 180–190°; the procedure of Pickard and Yates recommended boiling for 8–9 hours with dilute sulfuric acid (3:2). Combining these procedures, 88 g. of the nitrile was refluxed with 75% of sulfuric acid and 10 g. of sodium chloride with mechanical stirring for 22 hours and the product isolated in the usual way, b.p. 132° (3 mm.), m.p. 51–52°, recrystallized from an alcohol–water mixture (b.p. 161–163° (10 mm.), m.p. 52°[14]).

2-Phenylpentanol-1, not previously reported, was prepared by reduction of 120 g. (0.67 mole) of α-phenylvaleric acid with 32 g. (0.84 mole) of lithium aluminum hydride, b.p. 110° (6 mm.), n^{24}_D 1.5123, 91%.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.43; H, 9.98.

α-Phenylisovaleronitrile was prepared from benzyl cyanide by alkylation with sodium amide and isopropyl iodide according to the procedure described by Hancock and Cope.[12] From 246 g. (2.1 moles) of benzyl cyanide and 384 g. (2.26 moles) of isopropyl iodide there was obtained 263 g. (72%) of α-phenylisovaleronitrile, b.p. 106° (6 mm.), $n^{24.5}_D$ 1.5032 (b.p. 245–249° (765 mm.)[16]).

Anal. Calcd. for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 83.07; H, 8.38; N, 8.95.

2-Phenylisopentanol-1 was prepared by pouring a solution of 85 g. (0.48 mole) of phenylisopropylacetamide dissolved in one liter of absolute ethanol into 132 g. (5.7 moles) of clean sodium according to the procedure described for the preparation of 2-phenylbutanol-1.[3b] Originally the carbinol was to be prepared by lithium aluminum hydride reduction of the corresponding acid; however, hydrolysis of α-phenylisovaleronitrile, instead of going directly to the acid, yielded a product consisting almost entirely of the amide. This was of interest since the hydrolysis was carried out under conditions identical to those of the *n*-propyl compound in which the acid was obtained as the major product. The alcohol boiled at 93° (4 mm.), n^{21}_D 1.5160, 80% (b.p. 130° (15 mm.), no yield or refractive index,[3b] b.p. 130–132° (15 mm.), 66%, no refractive index,[3c] b.p. 127° (15 mm.) by reduction of the ethyl ester of dimethylatropic acid with sodium and alcohol[17]).

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.14; H, 9.75.

Acetylation of the Carbinols.—In a typical experiment, 95 g. (0.64 mole) of 2-phenyl-*n*-propylcarbinol, 153 g. (1.5 moles) or 142 ml. of acetic anhydride and 25 g. of sodium acetate was heated to boiling and allowed to reflux for 10 to 20 hours. The excess anhydride was decomposed carefully by the dropwise addition of water while the mixture was refluxing. An excess of water was then added, the solution was allowed to cool, and poured into a 2-liter separatory funnel. The solution was then washed several times with portions of 20% sodium carbonate, extracting with ether each time until carbon dioxide evolution stops, and then washed with water until the solution was neutral to litmus. The ether solution of the acetate was dried over anhydrous sodium sulfate, the ether removed, and the acetate distilled under reduced pressure through a 22-cm. Vigreux column.

The physical contents, yields and analyses of the acetates are listed in Table I.

α- and β-Alkyl Substituted Styrenes Prepared by Pyrolysis of the Acetates.—A procedure similar to the one for the pyrolysis of 2-alkyl-1,4-butanediol diacetates[18] was used with several experimental modifications. The α- and β-substituted acetates were added dropwise through a Pyrex glass tube (17 mm. i.d., 19 mm. o.d.) mounted vertically in an electric furnace, and packed with 6 × 6 mm. Raschig rings for 13 in., of which 12 in. were heated. The temperature of the "cracking oven" was obtained with the use of an iron–constant and thermocouple junction contained within a piece of glass tubing, and placed outside and halfway down the length of the column. The thermocouple was placed in this fashion since the pyrolysis was carried out at atmospheric pressure and it was necessary to have a closed system at the top of the column in order to force the vapors down into the receiving flask. Also, this eliminated any possibility of channeling which might occur if the thermocouple were placed inside the tube as described in reference 18. The receiving flask contained a side arm leading to the atmosphere and was cooled to Dry Ice temperatures. The drop time, oven temperature and yields are listed for various pyrolysis experiments in Table II.

After pyrolysis of the corresponding acetate, each monomer was distilled under reduced pressure through a Fenske type[19] total condensation-partial take off fractionating column, 53 cm. in height, 12 mm. i.d., packed with 1/8 in. glass helices and surrounded by an electrically heated jacket. The physical constants and analyses for the pure monomers are listed in Table III.

Ultraviolet Absorption Spectra.—Ultraviolet absorption spectra were determined with a Beckman quartz ultraviolet spectrophotometer using absolute ethanol as solvent. The data for the ultraviolet absorption spectra of styrene and the α- and β-alkyl substituted styrenes are given in Table IV, and the data for various fractions of β-methyl and β-ethyl styrene in Table V.

Attempted Isomerization of β-Alkylstyrenes.—A procedure similar to the one described for the isomerization of eugenol to isoeugenol[20] was attempted with β-methyl and β-ethyl styrene. The monomers (20 g.) were each weighed into a nickel crucible immersed in an oil-bath and powdered potassium hydroxide was added until it rose above the solution. The mixture was heated at 160° for 3.5 hours and then allowed to stand overnight. The solid "cake" which formed was ground in a mortar, extracted with ether, and distilled. There was no change in the boiling point or refractive index of either monomer indicating that the double bond was conjugated with the benzene ring.

A second procedure was used in which β-methylstyrene (n^{24}_D 1.5460) was dropped into a copper container containing solid potassium hydroxide pellets and heated in an oil-bath at 230°. The dropping funnel was connected to a copper tube which extended several inches below the potassium hydroxide so that the β-methylstyrene might bubble through the liquid alkali. The pressure of the system was sustained at 80 mm. and the β-methylstyrene removed at a rate of 30 drops per minute. The distillate was redistilled through a Vigreux-type column and the liquid showed no change in refractive index.

Ozonolysis of α-Alkyl Substituted Styrene Monomers.—The same procedure of ozonolysis was used for α-ethyl, α-*n*-propyl and α-isopropylstyrene. About 3% ozone was

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[15] A. Rossalymo, *Ber.*, **22**, 1235 (1889).

[16] F. Bodroux and F. Taboury, *Compt. rend.*, **150**, 531 (1910); *Bull. soc. chim.*, [4] **7**, 666 (1910).

[17] E. E. Blaise and A. Courtot, *ibid.*, [3] **35**, 505 (1906).

[18] C. G. Overberger, A. Fischman, C. W. Roberts, L. H. Arond and J. Lal, THIS JOURNAL, **73**, 2540 (1951).

[19] T. P. Carney, "Laboratory Fractional Distillation," The Macmillan Company, New York, N. Y., 1949, pp. 111-115.

[20] S. J. Gokhole, J. J. Sudborough and H. E. Watson, *J. Indian Inst. Sci.*, **6**, 241 (1923).

passed through a solution of 2 g. of the monomer dissolved in 50 ml. of ethyl acetate until the reaction was complete. The reaction mixture was kept at Dry Ice temperatures to prevent the loss of any formaldehyde which might be liberated during the course of the reaction. The reaction time of each experiment was approximately 45 minutes. Decomposition of the ozonide was carried out by a procedure similar to that of Hurd and Blanchard[21] in which the ozonide was poured into 50 ml. of water and 10 g. of zinc dust and the mixture mechanically shaken for 20 minutes. The zinc dust was collected on a filter and the water layer separated from the organic layer in a separatory funnel. To the former there was added a solution of 36.4 g. (0.026 mole) of methone dissolved in 25 ml. of 50% ethanol and to the latter there was added a solution of 2.57 g. (0.13 mole) of 2,4-dinitrophenylhydrazine dissolved in 20 ml. of concentrated sulfuric acid to which was added 20 ml. of water. Crystals separated almost immediately in all experiments. The methone derivatives were recrystallized from 95% ethanol and ethyl acetate mixtures. The melting points and yields of the derivatives of the ozonide decomposition products for the three monomers were as follows: α-ethylstyrene, methone derivative, m.p. 189°, 59%; 2,4-dinitrophenylhydrazone, m.p. 190–191°, 45% (formaldehyde dimethone, m.p. 189°; ethyl phenyl ketone 2,4-dinitrophenylhydrazone, 191°)[22]; α-*n*-propylstyrene, methone derivative m.p. 188.5–189°, 52%; 2,4-dinitrophenylhydrazone, m.p. 189–190°, 57% (*n*-propyl phenyl ketone, 2,4-dinitrophenylhydrazone, m.p. 188 or 190°)[22]; α-isopropylstyrene, methone derivative, m.p. 189°, 53%; 2,4-dinitrophenylhydrazone, m.p. 157–158°, 62% (isopropylphenyl ketone, 2,4-dinitrophenylhydrazone, m.p. 163°.[22]

A mixture of methone derivatives from the ozonide decomposition products of the α-ethyl, α-propyl and α-isopropylstyrenes were mixed together with formaldehyde dimethone, m.p. 189°, with no depression of the melting point.

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BROOKLYN, N. Y.

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[21] C. D. Hurd and C. A. Blanchard, THIS JOURNAL, **72**, 1461 (1950).

[22] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941.

[CONTRIBUTION FROM INSTITUTE OF POLYTECHNICS, OSAKA CITY UNIVERSITY]

Absorption Spectra and Chemical Structures. I. Conjugated Polyenes and *p*-Polyphenyls

BY KENZÔ HIRAYAMA

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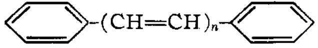
A study is presented of the dependence of spectral absorption on structure in polyene derivatives and *p*-polyphenyls. In this paper conjugation of similar chromophoric groups is considered. It is shown that the wave length of the first absorption maximum may be expressed by $(\lambda_{\max})^2 = A - BC^N$, where N is a proposed index defined by number of conjugated homochromophores, number and type of substituents, and of spectroscopically effective structures.

It has long been known that definite relationships exist between the structure of organic molecules and their visible and ultraviolet absorption spectra; empirical and theoretical formulas have been advanced relating the wave length of the first absorption maximum with the number of conjugated chromophoric groups.

But the values calculated by these formulas do not always agree satisfactorily with the observed values. However, we have found that the wave lengths predicted by equation 1,[1] in which n is the number of conjugated groups, agreed well with the observed wave lengths of the first absorption maximum.

$$(\lambda_{\max})^2 = a + B(1 - C^n) = A - BC^n \qquad (1)$$
$$(A = a + B)$$

The adequacy of this functional relationship is shown in the following examples.

α,ω-Diphenylpolyenes: 

For benzene solutions, equation 2 holds

$$(\lambda^{\text{benz}}_{\max})^2 = (38.08 - 30.81 \times 0.934^n) \times 10^4 \text{ m}\mu^2 \qquad (2)$$

The values in column *a* of Table I calculated by equation 2 are more satisfactory than those in column *b* calculated by Lewis and Calvin's formula 3[2]

$$(\lambda_{\max})^2 = A + Bn \qquad (3)$$

or the values in columns *c* and *d* given by Dewar's LCAO MO method.[3]

In spite of the comparative agreement between the values in column *b* and those observed, equation 3 is not valid because the relation between λ^2 and n is obviously not linear[4] (see Fig. 1).

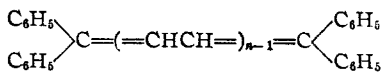
TABLE I

ABSORPTION MAXIMA OF α,ω-DIPHENYLPOLYENES IN BENZENE

	Obsd.,[a]	Calcd.			
n	mμ	*a*, mμ	*b*, mμ	*c*, mμ	*d*, mμ
1	306	305	310	311	256
2	334	335	334	357	294
3	358	360	358	412	339
4	384	382.5	380	445	366
5	403	402	400	480	395
6	420	420	420	505	416
7	435	435.5	438.5	532	438

[a] K. W. Hausser, R. Kuhn and A. Smakula, *Z. physik. Chem.*, B29, 384 (1935).

α,α,ω,ω-Tetraphenylpolyenes:



$$(C_6H_5)_2C{=}({=}CHCH{=})_{n-1}{=}C(C_6H_5)_2$$

Equation 4 holds for this series; the agreement between the values for the parameter C in equations 2 (C 0.934) and 4 (C 0.935) should be noted. The

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[1] One possible justification for the functional relation (1) will be demonstrated in the appendix.

[2] G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 273 (1939).

[3] M. J. S. Dewar, *J. Chem. Soc.*, 3544 (1952).

[4] Nevertheless, since the numerical disagreement between the values obtained by equations 2 and 3 are so slight, it may be conceded that the results obtained with the Lewis and Calvin equation are superior in the sense that the latter was derived on the basis of a physically significant model. Thus far, our equation has been described merely as an empirical relation. In the appendix, however, a justification of the new relation is given.