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A Comparative Study of the Three Stereoisomeric 1,4-Diphenylbutadienes

BY J. H. PINCKARD, B. WILLE AND L. ZECHMEISTER

It was recently shown, in collaboration with A. Sandoval,[1] that the maximum extinction in the spectrum of ordinary *trans-trans*-1,4-diphenylbutadiene, $C_6H_5CH{=}CHCH{=}CHC_6H_5$, decreased to about half of the original value upon illumination under certain conditions. However, almost entire restoration of the original extinction curve by iodine catalysis proved that no irreversible destruction had taken place. Further experiments for the identification of the chromatographically homogeneous product were announced.

As is known, Straus[2] prepared two stereoisomers of diphenylbutadiene by reduction methods; one was crystalline (m. p. 70.5°, compared to 152–153°, cor., of the *trans–trans* form) and the other was oily. We were able to confirm Straus' data concerning the crystalline compound but have observed by chromatography that the oily sample contains a number of impurities. After their elimination on the Tswett column, this isomer was found to be identical with that obtained photochemically.[1] Of course, illumination is a simpler method of preparing this oily isomer than the reduction of *trans*-diphenylbutenine.[2]

It was observed in the field of the carotenoids[3] that a single *trans* → *cis* rotation shifts the position of $\lambda_{\max.}$ by about 7.5 mμ toward shorter wave lengths (*e. g.*, lycopene, in hexane, measured in the Beckman spectrophotometer). We noticed a similar shift when the extinction curves of the three diphenylbutadienes were compared in hexane solution; however, in this case one *trans* → *cis* step causes a wave length difference of 14–15 mμ:

trans–trans form (m. p. 152–153°), $\lambda_{\max.}$ at 328 mμ
cis–trans form (oily), $\lambda_{\max.}$ at 313 mμ
cis–cis form (m. p. 70.5°), $\lambda_{\max.}$ at 299 mμ

These data compare well with those referring to *trans*- and *cis*-stilbene (difference in $\lambda_{\max.}$, 15 mμ)[4] and they also agree with the assignment of configurations to stereoisomeric diphenylbutadienes as given by Straus. An absolute structure determination of *cis–cis*-diphenylbutadiene is not yet available.[2a]

The extinction curve of *trans-trans*-diphenylbutadiene shows definite fine structure while the two other isomers are characterized by smooth curves which are rather similar in this respect (Figs. 1–2).

When petroleum ether is used as a developer, the chromatographic sequence on alumina from top to bottom is: *trans-trans-*, *cis-trans-*, and *cis-cis*-diphenylbutadiene. The zone of the *trans-trans* form can be located by its intense bluish fluorescence in ultraviolet light. The presence of one or two *cis* double bonds, however, destroys this power to fluoresce, in adsorbate as well as in solution. On the other hand, zones of the *cis-trans* and *cis-cis* forms, when either is present in appreciable quantity, may be located on the column by the moderate quenching of the weak fluorescence of the alumina itself. Like *cis-* and *trans*-stilbene zones,[5] those of the three diphenylbutadienes are also detected by brushing with permanganate.

A sharp separation of the *cis-trans* and *cis-cis* forms can be accomplished by means of the liquid chromatogram procedure. The detection of either isomer in the successive fractions of the filtrate is carried out by treating small samples of each fraction with catalytic amounts of iodine followed by a brief illumination. Thus, either of these two stereoisomers is converted into the *trans-trans* form, whereupon fluorescence appears in the solution when inspected in ultraviolet light. The limit of detection is 0.5–1.0 milligram per liter or a few micrograms in a 2-ml. test sample. The recovery of each of the three stereoisomers from artificial mixtures was practically quantitative in such resolutions.

Having chromatographically pure samples of all stereoisomeric diphenylbutadienes, a comparison of their behavior under various conditions was made; the result may be summarized as follows.

In petroleum ether, at 4°, and in the absence of light any of the three configurations can be preserved for several months. When hexane solutions are refluxed in all-glass apparatus, in darkness, for forty-five minutes, the three stereoisomers behave identically: their extinction curves were practically unchanged. The isomers showed only a limited difference when kept in the molten state at 205° for ten minutes, with the exclusion of air and light. The *trans-trans* and *cis-trans* configurations were practically unaffected; *cis-cis*-diphenylbutadiene underwent moderate isomerization whereby the amount of the *trans-trans* compound formed did not exceed 5%.

In order to test the relative photo-stabilities, we conducted two series of experiments under very different conditions: (*a*) illumination of the hexane solution (20 mg. per liter) in Pyrex flasks with a 250-watt light bulb for several hours, and

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(1) A. Sandoval and L. Zechmeister, THIS JOURNAL, **69**, 553 (1947).

(2) F. Straus, *Ann.*, **342**, 190 (1905), *cf.* C. Kelber and A. Schwarz, *Ber.*, **45**, 1946 (1912); E. Ott and R. Schröter, *ibid.*, **60**, 624 (1927).

(2a) Dr. E. W. Hughes is carrying out a preliminary X-ray examination in these laboratories.

(3) Summary: L. Zechmeister, *Chem. Rev.*, **34**, 267 (1944).

(4) A. Smakula and A. Wassermann, *Z. physik. Chem.*, **A155**, 353 (1931).

(5) L. Zechmeister and W. H. McNeely, THIS JOURNAL, **64**, 1919 (1942).

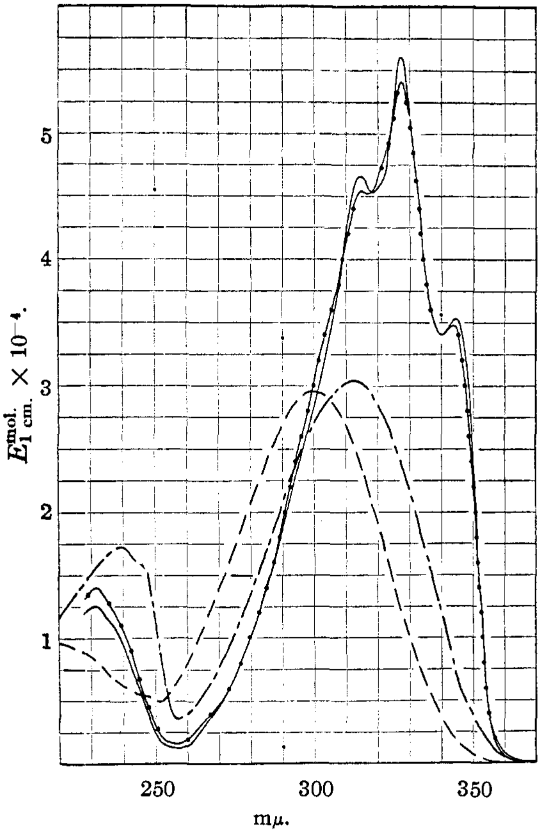

Fig. 1.—Molecular extinction curves of the three stereoisomeric diphenylbutadienes in hexane: —, *trans–trans* compound; — — — —, *cis–trans* compound; - - - -, *cis–cis* compound; —●—●—, after iodine catalysis of any of the foregoing solutions.

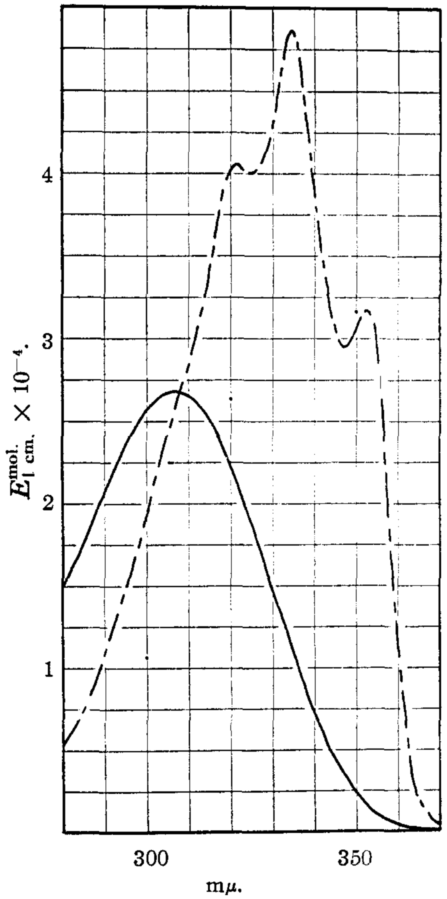

Fig. 2.—Molecular extinction curve of *cis–cis*-diphenylbutadiene in benzene: —, fresh solution; — — — —, after iodine catalysis.

(*b*) insolation, *i. e.*, exposure of more dilute solutions (3–4 mg. per liter) to intense sunshine, in transparent quartz tubes, for one to ten minutes.

In the (*a*) series it was found that the extinction curve of *cis-trans*-diphenylbutadiene was practically unchanged, even after seventeen hours of illumination; the two other isomers underwent almost quantitative rearrangement, and at the end of the irradiation period also showed very nearly the spectral curve of the *cis-trans* form (Figs. 3–4). The *trans-trans* isomer required only one to two hours to reach this state but the *cis-cis* compound as long as thirteen to fourteen hours.

During the insolation as shown by Fig. 5, the fine structure of the *trans-trans* curve had almost entirely disappeared after one minute and the extinction curve approached closely that of the *cis-trans* isomer after ten minutes. The *cis-cis* configuration underwent a similar rearrangement essentially to the *cis-trans* form (Fig. 6), while no appreciable change in the extinction curve was noticed after *cis-trans*-diphenylbutadiene had been insolated for ten minutes.

Whether or not irreversible processes also take place besides photo-isomerization, is revealed by subsequent iodine catalysis and brief illumination with a daylight lamp. If the molecular extinction coefficient at $\lambda_{\text{max.}}$ is then found to be smaller than the value established earlier by a similar catalytic treatment of the *trans-trans* form, then the deficit is a fair measure of photochemical destruction. In the experiments with artificial light such losses were smaller than 1–2% of the starting material; however, they amounted to about 8–10% after ten minutes of insolation.

Special experiments showed that upon iodine catalysis in light (like the carotenoids) the stereoisomeric diphenylbutadienes yield practically identical mixtures which in this case contain about 97% all-*trans* form. However, if iodine is added in darkness to the solution, none of the diphenylbutadienes shows a detectable spectral change within half an hour. A subsequent exposure of the *cis-cis* compound even for as little as twenty seconds to the daylight lamp caused noticeable rearrangement. Figure 7 shows, both in the fundamental band and in the secondary maximum near 230 mμ, that the main process in the first stages is a stepwise conversion, *cis-cis* → *cis-trans* → *trans-trans*. If a direct *cis-cis* → *trans-*

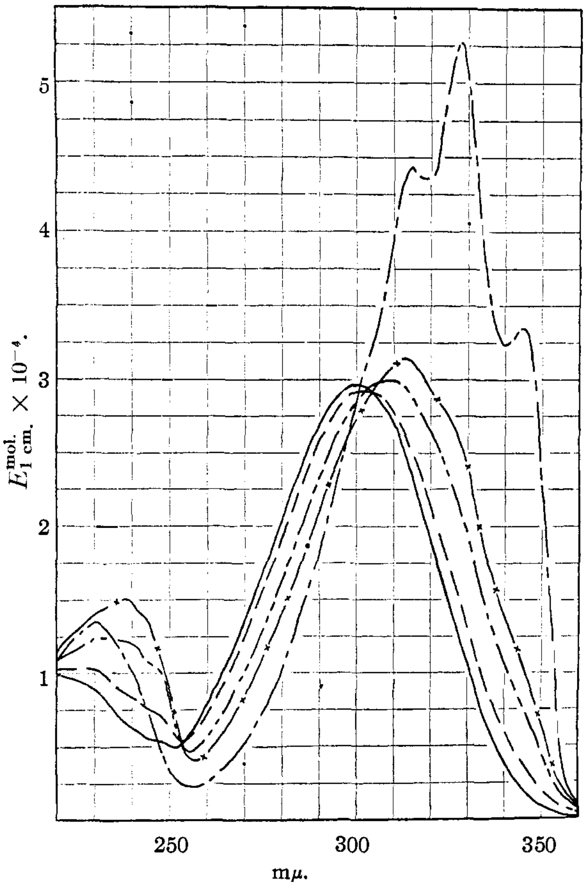

Fig. 3.—Molecular extinction curve of *cis–cis*-diphenylbutadiene in hexane, and its gradual shift toward the curve of the *cis–trans* form during illumination with a 250-watt bulb: —, fresh solution of the *cis–cis* compound; — — —, after forty-five minutes; — - — -, three hours and forty-five minutes; and — x — x —, seventeen hours of illumination; — — — —, after iodine catalysis at the end of seventeen hours of illumination.

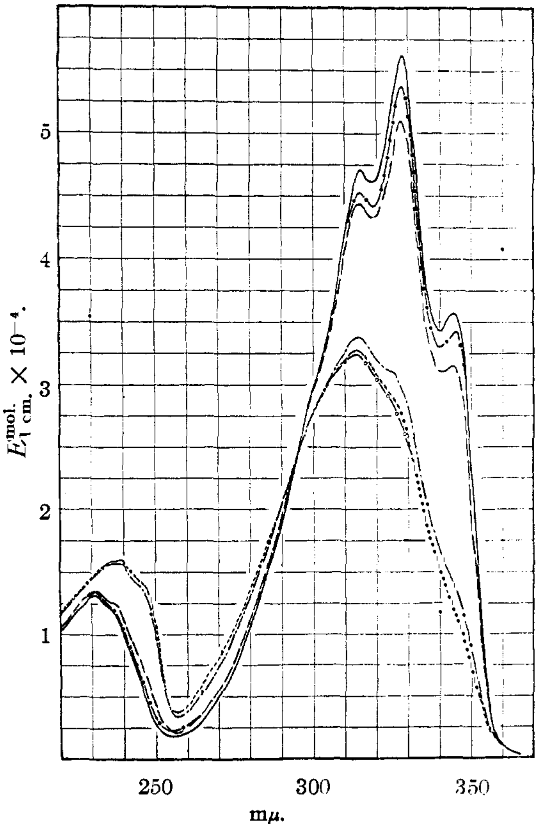

Fig. 4.—Molecular extinction curve of *trans–trans*-diphenylbutadiene in hexane, and its gradual shift toward the curve of the *cis–trans* form during illumination with a 250-watt bulb (strictly parallel experiment to that represented in Fig. 3): —, fresh solution of the *trans–trans* compound; — — —, after fifteen minutes; — · — ·, forty-five minutes; - - - -, one hour and forty-five minutes; — O — O —, eight hours illumination; —●—●—, after iodine catalysis at the end of seventeen hours of illumination.

trans rearrangement took place, one would expect the appearance of some fine structure in early stages of the illumination; even the presence of 5% *trans-trans* form gives rise to recognizable bulges in the extinction curve, especially around 328 mμ and 344 mμ (in hexane). On the other hand, after illumination for twenty-five minutes the curve in Fig. 7 is essentially that of *trans-trans*-diphenylbutadiene.

The height of $E_{\text{max.}}$ also indicates that only a spatial change and no destruction took place. In contrast, when the addition of iodine is followed by excessive illumination, irreversible processes also occur, for example to the extent of 30% during a six-hour exposure to the 250-watt bulb. In the absence of iodine there is no destruction under the same conditions.

Finally, the stability of the three isomers in the absence of solvents was investigated. The oily *cis-trans* compound has the tendency, even in almost complete darkness, to rearrange and deposit crystals of the *trans-trans* isomer; in strong light such crystals appear within a minute.[6,2] Although the oil was handled cautiously, its crystallization tendency was always found to be inferior to its inclination for the spatial change. So far we have failed to obtain *cis-trans*-diphenylbutadiene in crystalline form.

The present study should show that, from the viewpoint of the practical chemist, no one of the three configurations of diphenylbutadiene is the most stable under all conditions. While photochemically the *trans-trans* and the *cis-cis* forms proved to be labile and changed their configuration to *cis-trans*, the latter is much less stable than the others in the absence of solvents. Under none of the conditions tested was the *cis-cis* form the most stable. However, at room temperature the stability of its crystals compared well with the crystalline *trans-trans* compound, and these two forms show no great difference even at 205°.

(6) Reference 1, Fig. 8.

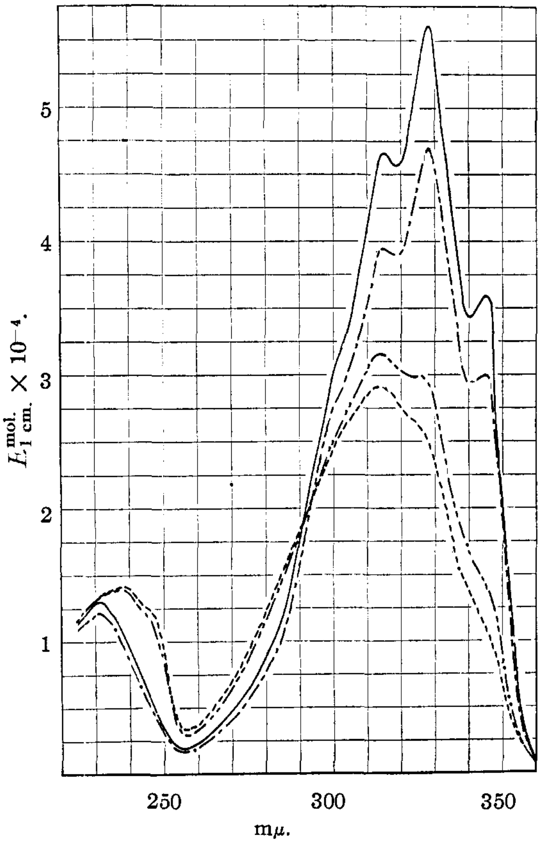

Fig. 5.—Molecular extinction curve of *trans–trans*-diphenylbutadiene in hexane, and its shift toward the curve of the *cis–trans* form during exposure to sunshine: —, fresh solution; – – – –, after one minute; – – – –, ten minutes of insolation; — · — ·, after iodine catalysis at the end of ten minutes of insolation.

Some distinctly individual features of *cis-trans*-diphenylbutadiene as compared to its stereoisomers are also revealed by an inspection of the three models. The dotted lines in Fig. 8 which connect the ends of each resonating system, demonstrate the essentially linear shape of the *trans-trans* and *cis-cis* molecules while the *cis-trans* form shows the pattern of a widely open V. Comparable forms of carotenoids would be[7]; lycopene, neolycopene A, and poly-*cis*-lycopene "IV" (or another poly-*cis*-lycopene).[8] Neolycopene A is characterized by lability of its configuration in the absence of solvents, lack of crystallization tendency (without rearrangement), and by its high *cis*-peak. Although no clearly differentiated *cis*-peak appears in the relatively compressed spectral curve of *cis-trans*-diphenylbutadiene, its extinction at 230 to 240 mμ is the highest of all three stereoisomers. Furthermore, its maximum is located at a 9 mμ longer wave length than the corresponding maximum of the *trans-trans* compound. On the other hand, *cis-cis*-diphenylbutadiene can be compared with a poly-*cis*-lycopene: both show a flat section of the extinction curve in the (potential) *cis*-peak region.

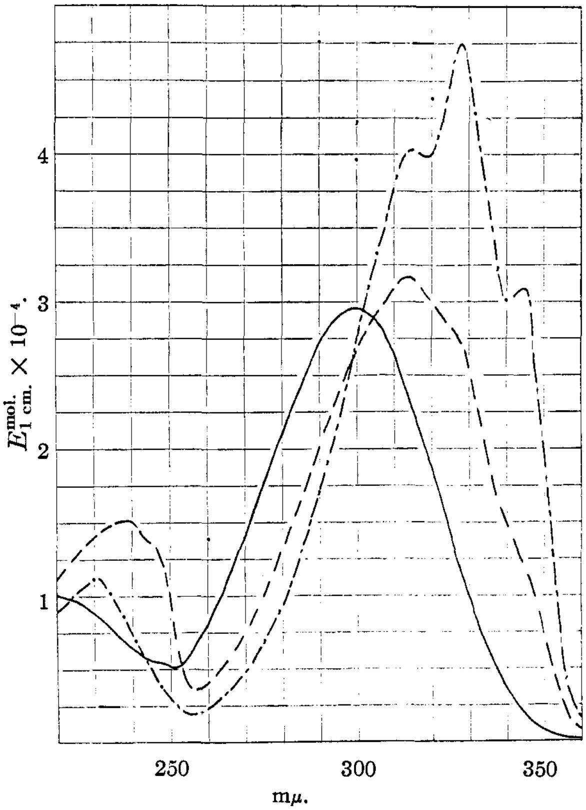

Fig. 6.—Molecular extinction curve of *cis–cis*-diphenylbutadiene in hexane, and its shift toward the curve of the *cis–trans* form during exposure to sunshine: —, fresh solution; – – – –, after ten minutes of insolation; — · — ·, after iodine catalysis at the end of ten minutes of insolation.

Although extinction areas are more characteristic than the height of maxima, the following data show the very great decrease in $E_{max.}$ when several *cis* double bonds are formed by rearrangement; and they also indicate that the first *trans* → *cis* step is responsible for the major part of this effect: Relative heights of $E_{max.}$ in hexane (per cent.): all-*trans*-lycopene, 100; neolycopene A (a central mono*cis* lycopene), 66; poly-*cis*-lycopene "IV," 56; *trans-trans*-diphenylbutadiene, 100; *cis-trans*, 54; and *cis-cis*, 53.

The lack of fine structure in the extinction curve of *cis-trans* or *cis-cis*-diphenylbutadiene parallels to a certain extent the recent observation that all poly-*cis*-lycopenes known at the present time show a very limited fine structure when compared to that of the all-*trans* form.[8]

Acknowledgment.—The authors wish to thank Professor A. J. Haagen-Smit as well as Dr. G. Oppenheimer and Mr. G. Swinehart for microanalyses.

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(7) L. Zechmeister, A. L. LeRosen, W. A. Schroeder, A. Polgár and L. Pauling, THIS JOURNAL, **65**, 1940 (1943).

(8) L. Zechmeister and J. H. Pinckard, *ibid.*, **69**, 1930 (1947).

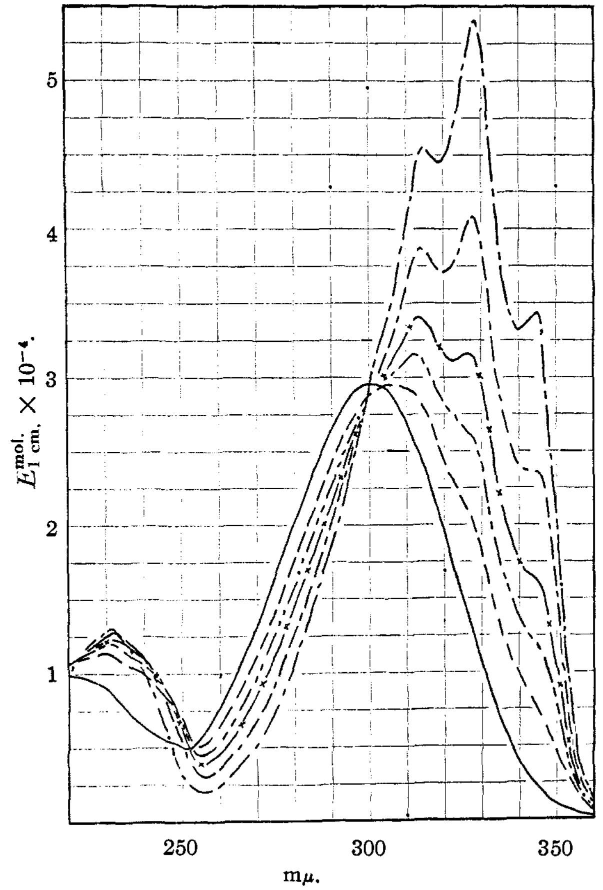

Fig. 7.—Molecular extinction curves in hexane; influence of illumination on the stereoisomerization of *cis–cis*-diphenylbutadiene caused by iodine catalysis: —, fresh solution with iodine, kept in darkness for thirty minutes; - - - -, after eighty seconds; — — — —, one hundred and forty seconds; — x — x —, 200 seconds; — — — — — —, 320 seconds; and — - — -, 25 minutes illumination.

Experimental

Adsorbents and Solvents.—"Silicic acid" means Merck reagent silicic acid plus 20% celite. Commercial alumina (Alorco, Grade F, ground to –200 mesh) was used mixed with 25% celite. On such columns 0.5% permanganate is a suitable color reagent for the location of diphenylbutadiene zones by brushing.[5] The petroleum ether was Skellysolve B, b. p. 60–70°. The hexane was prepared from Phillips commercial brand by repeated treatment with fuming sulfuric acid.

Light Sources and Conditions of Illumination.—Chromatograms were inspected in the light of a General Electric Purple X bulb using a moulded Corning light filter No. 5840, 0.25 inch thick; "Mineralight Q31" was less satisfactory due to its different light filter. The conditions for the illumination of iodine catalyzed solutions with a Mazda daylight lamp were described in detail recently.[1] Under the same conditions benzene solutions should be illuminated for an hour. For artificial illumination of iodine-free solutions a 250-watt Mazda clear projection lamp bulb (Code –250 T 14/3 –120V) encased in a water jacket was used (distance from filament to center of Pyrex volumetric flask, 10 cm.). Transparent quartz test-tubes were found satisfactory for insolation experiments (end temperature, 20–25°). The values for each extinction curve, taken in the Beckman photoelectric spectrophotometer, are based on the average of at least two independent determinations.

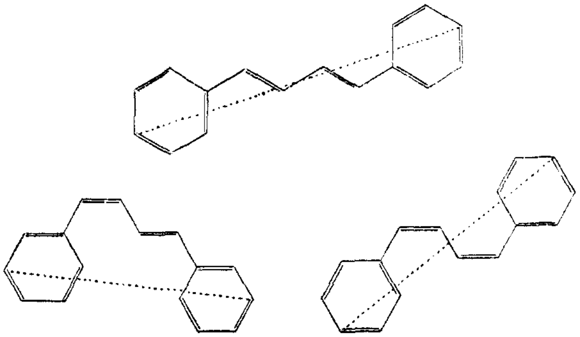

Fig. 8.—Models of *trans–trans-* (top), *cis–trans-* (bottom, left), and *cis–cis*-diphenylbutadiene (bottom, right). (Values: C=C, 1.33 Å.; C—C, 1.46 Å.; and C=C—C angle, 124° 20′. The dotted lines connect the ends of each resonating system.)

Thermal Treatment.—Refluxing of hexane solutions (5–20 mg. per liter) was carried out in darkness, in a slow stream of carbon dioxide. In the melt experiments, 4–12 mg. weighed samples, in evacuated and sealed capillary tubes, were submerged in a dibutyl phthalate bath (205–210°), in darkness. After ten minutes the tubes were rapidly cooled in water and their contents examined without delay.

***trans*-Diphenylbutenine**, $C_6H_5CH{=}CHC{\equiv}CC_6H_5$, was prepared (in a crude state) from phenylacetylene–copper according to Straus.[2] Purification: a solution of 8.5 g. of brownish, crude crystals in 100 ml. of petroleum ether was developed with the same solvent on a silicic acid column, 22 × 4.8 cm. (The figures on the left designate thickness of the zones in mm.; fl. means fluorescence or fluorescent in ultraviolet light):

30	several brown zones (in daylight)
30	white fl. (1 g. oil)
7	brown (in daylight)
8	interzone, no fl.
50	white fl. (1 g. oil)
80	column-fl. quenched: main product
Filtrate: no fl.	

The main zone was cut out, eluted with ethanol, transferred into petroleum ether, dried with sodium sulfate and completely evaporated *in vacuo*. A solution of the slightly colored crystals (5.5 g.) in 50 ml. of hot methanol deposited 3 g. of white needles in the cold room; m. p. 96°, cor. An additional 1 g. can be obtained by chromatographing the mother liquor as above.

***cis–trans*-Diphenylbutadiene from *trans*-Diphenylbutenine.**—In an all-glass apparatus (with mercury-sealed stirrer) the solution of 3 g. of the butenine in 250 ml. of alcohol was refluxed in darkness with 2 g. of zinc–copper dust (from copper sulfate and zinc, washed with ethanol) and another 2 g.-portion of the metals was introduced after thirty hours. The sharp extinction maximum (originally at 306 mμ., in petroleum ether) gradually disappeared and, after one hundred and ten hours of refluxing, the smooth maximum of *cis–trans*-diphenylbutadiene was observed in a small sample. Then 250 ml. of petroleum ether and 1 liter of water were added to the filtered liquid; the aqueous layer was re-extracted and the total petroleum ether solution was repeatedly washed and dried. The following chromatogram, obtained with the same solvent, on a 28 × 8 cm. alumina column, refers to one third of the crude solution:

30	several, partly fl. zones
25	blue fl.: *trans-trans*-diphenylbutadiene
140	fl. of alumina quenched: crude *cis-trans*

When the bottom of the lowest zone was 7 cm. from the end of the column, the quenched section was cut out in two halves of which the upper one contained unchanged butenine (its extinction curve was not influenced by iodine). The bottom half of the quenched zone showed the spectroscopic character of *cis-trans*-diphenylbutadiene, and a sample yielded (after iodine catalysis in light) the fine structure of the *trans-trans* form. This fraction was rechromatographed as above.

In order to eliminate the last impurities, especially for optical observations, 3 mg. of the *cis-trans* compound (in 3 ml. of petroleum ether) was adsorbed on a 20 × 1.9 cm.-column and washed with the same solvent. Each 10-ml. portion of the (non-fluorescing) filtrate was tested as follows: A few drops were catalyzed with one drop of iodine solution (0.3 mg./ml.) and the test-tube exposed to the 250-watt lamp from a 10 cm. distance for one to two minutes. If the sample showed fluorescence in ultraviolet light, the fraction was kept, otherwise rejected. This test was positive between the fractions 17–29. Fractions 18–28 were found spectroscopically to contain pure *cis-trans* compound; 3 g. of the butenine yielded 0.75 g. of the purest product.

The molecular extinction coefficients were given earlier.[9]

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 92.73, 92.89; H, 6.84, 6.88.

***cis-cis*-Diphenylbutadiene** was prepared by catalytic reduction of diphenyldiacetylene, $C_6H_5C{\equiv}CC{\equiv}CC_6H_5$, by Kelber and Schwarz as well as by Ott and Schröter[2] in yields of 8–32%, depending on the catalyst. Although our yields remained between these limits (for example, 24%), we recommend the following isolation which is based on spectroscopic control of the reduction process and chromatographic purification of the product. During the reaction the triple bonds are reduced not only to double, but in part also to single bonds. These competing processes can be followed by the changing extinction curve. The sharp and high peaks of diphenyldiacetylene at 306 and 326 mμ. (in hexane) gradually disappear and the much lower, smooth maximum of *cis-cis*-diphenylbutadiene at 300 mμ. then makes the main contribution to the curve. A satisfactory amount of the latter compound is clearly indicated if a small sample (diluted with hexane) is examined in the spectrophotometer before and after iodine catalysis (in light). The new maximum (now at 328 mμ.) should be at least 1.5 times higher than $E_{max.}$ was before this catalytic treatment.

Fig. 9.—Crystals of *cis–cis*-diphenylbutadiene (from methanol).

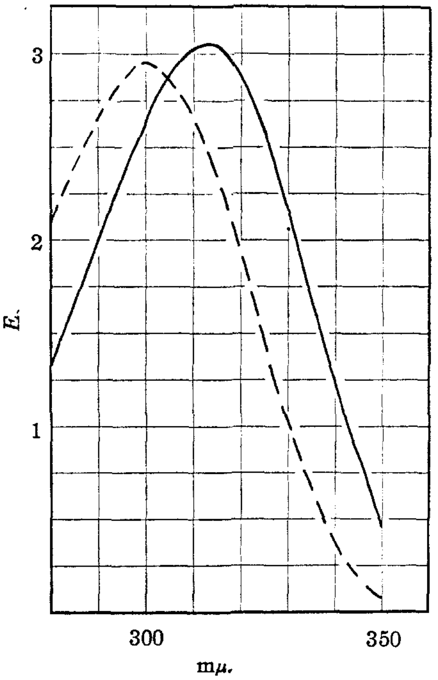

Fig. 10.—Extinction curves (main maxima only) of *cis–cis*- and *cis–trans*-diphenylbutadiene in petroleum ether as obtained by the resolution of their mixture in a liquid chromatogram experiment: — — —, *cis-cis*- and ——, *cis–trans*-diphenylbutadiene.

The following operations should be carried out in dim light. A solution of 1 g. of diphenyldiacetylene in 100 ml. of 95% ethanol was shaken with 0.25 g. of palladium-barium sulfate[10] until roughly 350 ml. of hydrogen was taken up within one quarter to one half hour. After filtration, the material was transferred with water into petroleum ether and the aqueous phase re-extracted. The combined petroleum ether solution, after washing, drying and concentrating to 50 ml., was developed on an alumina column (30 × 7.5 cm.) with about 2 liters of the same solvent:

6	dark (in uviol. light)
8	greenish fl.
20	blue fl.: *trans-trans*-diphenylbutadiene
16	non-fl. interzone
60	column-fl. quenched: *cis-trans*-diphenylbutadiene
26	interzone (borders blurred)
50	column-fl. quenched: *cis-cis*- diphenylbutadiene
110	empty section

The location of the *cis-cis* compound possibly could be improved by using a strongly fluorescent column as proposed by Sease.[11]

The *cis-cis* zone was cut out, eluted with ethanol, transferred into petroleum ether, washed, dried and completely evaporated *in vacuo*. The oily residue was then transferred into a small centrifuge tube and dissolved in a minimum amount of warm 95% ethanol. Crystallization was observed at room temperature, whereupon the tube was kept at 4° overnight. Yield, after recrystallization, was 243 mg. of *cis-cis*-diphenylbutadiene which showed distinctly different crystal forms (Fig. 9) from those of the *trans-trans* isomer.[12] The extinction coefficients are given in Table I.

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[9] Reference 1, p. 555, Table I; the term "chromatographically homogeneous *cis* form" should now be replaced by "*cis-trans*-diphenylbutadiene." The "All-*trans* form" in the same table refers to *trans-trans*-diphenylbutadiene.

[10] "Organic Syntheses," **26**, 77 (1946).

[11] J. H. Sease, THIS JOURNAL, **69**, 2242 (1947); H. Brockmann and F. Volpers, *Ber.*, **80**, 77 (1947).

[12] Reference 1, Fig. 8.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.13; H, 7.17.

TABLE I

MOLECULAR EXTINCTION COEFFICIENTS OF *cis-cis*-DIPHENYLBUTADIENE AT THE MAXIMA (*italicized*) AND MINIMA

Solvent	*cis-cis* form mμ	$E^{\text{mol.}}_{1\text{ cm.}} \times 10^{-4}$	Mixture of stereoisomers upon iodine catalysis mμ	$E^{\text{mol.}}_{1\text{ cm.}} \times 10^{-4}$
Hexane	*299–300*	2.96	*344–345*	3.40
	251	0.51	340	3.35
			328	5.36
			318–319	4.50
			315–316	4.56
			255	0.20
			230–231	1.36
Benzene	*306*	2.67	*352–353*	3.17
			347	2.95
			334–335	4.85
			325–326	4.00
			321–322	4,05

Small-Scale Separation of the Three Stereoisomeric Diphenylbutadienes.—A solution which contained 1 mg. of each isomer in 10 ml. of petroleum ether was developed with the same solvent on alumina (20 × 2 cm.); the developer was forced through the column by nitrogen pressure in order to avoid partial evaporation of the filtrate. The fluorescent *trans-trans* compound remained near the top. Small samples of each fraction collected from the filtrate were submitted to the iodine-catalysis and fluorescence test as described. The first 120 ml. of the flow were found to be free of substance; subsequent 5-ml. fractions were tested with the following result ("*cis-cis*" or "*cis-trans*" refer to the configuration before iodine catalysis):

No. 1–7, strong fl.: *cis-cis*
8–9, weak fl.: *cis-cis*
10–12, almost no fl.: traces
13–21, very strong fl.: *cis-trans*
22–26, strong fl.: *cis-trans*
27–30, weak fl.: *cis-trans*
31, no fl.

The fractions were also tested spectroscopically; the extinction curves of fractions 3 and 16 are given in Fig. 10.

Summary

A comparative study of the *trans-trans-*, *cis-trans-*, and *cis-cis-* forms of 1,4-diphenylbutadiene is presented. The relative stability of the respective configurations depends on the nature of the photochemical or thermal treatment. Data characterizing the spectroscopic and chromatographic behavior are given, and the stereoisomeric diphenylbutadienes are compared with some spatial types of the carotenoids.

PASADENA, CALIFORNIA RECEIVED DECEMBER 20, 1947

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WESTERN AUSTRALIA]

Isopiestic Measurements on the Primary Sodium and Potassium Salts of Malonic, Succinic and Adipic Acids at 25°

BY JEAN M. STOKES[1]

The order of the activity coefficient curves for the alkali formates, acetates, and hydroxides is Li < Na < K, a reversal of the usual order K < Na < Li which holds for the halides and many other salts. To account for this, Robinson and Harned[1a] have advanced an hypothesis of "localized hydrolysis," according to which anion and cation are "associated" through interaction with a polarized water molecule, an effect which may be expected to depend on the proton-accepting power of the anion. In order to study this effect for salts of acids of different strengths, the primary sodium and potassium phosphates have been investigated.[2] It was found, however, that these two salts had very low activity coefficients and ionic association probably occurred to a marked extent. Indeed, the primary phosphate ion seems to belong to what Scatchard[3] has termed the second class of anions, in which he included the nitrate, chlorate and perchlorate ions and to which recent measurements[4] indicate the bromate ion should be added.

Measurements are now reported on the salts of three acids of dissociation constant ranging from 10^{-3} to 10^{-5}.

Experimental

Solutions of the sodium and potassium salts of malonic, succinic and adipic acid were prepared by (a) half neutralization of the purified acid with hydroxide in aqueous solution and (b) precipitation of solid salt from alcoholic solutions of acid and base, digestion with alcohol and subsequent solution in water. The two methods gave similar results but the experimental points did not lie on a smooth isopiestic curve as well as other salts that have been investigated. This may be due to sensitivity to the exact composition of the alkali hydrogen salt or to the *p*H of the solution; high accuracy is not claimed for these results, but they are probably accurate to 1% and the order and position of the activity coefficient curves is therefore significant. The molalities of isopiestic solutions are given in Table I and the osmotic and activity coefficients calculated with the aid of the data for the reference salt, sodium chloride,[5] are given in Table II.

Discussion

The activity coefficient curve of sodium hydrogen adipate is close to that of potassium iodide while the potassium salt resembles potassium bromide; sodium and potassium hydrogen succinate are comparable with rubidium chloride and cesium bromide, respectively; sodium hydrogen malo-

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