significance to the great problem of the nature of the metallic state will be communicated later.

Acknowledgment.—The work reported in this paper is part of a series of studies of metals and alloys being carried on with the aid of a grant from the Carbide and Carbon Chemicals Corporation.

Summary

An equation has been formulated to express the change in covalent radius (metallic radius) of an atom with change in bond number (or in coördination number, if the valence remains constant), the stabilizing (bond-shortening) effect of the resonance of shared-electron-pair bonds among alternative positions being also taken into consideration. This equation has been applied to the empirical interatomic-distance data for the elementary metals to obtain a nearly complete set of single-bond radii. These radii have been compared with the normal covalent radii, tetrahedral radii, and octahedral radii of the elements; their evident close relationship strongly supports the idea that the interatomic forces in metals are for the most part due to covalent bonds resonating among the available interatomic positions.

It is found that chromium atoms, manganese atoms, and tin atoms exist in metals in two forms, a small, high-valent form and a larger, low-valent form. The two kinds of manganese atoms coexist in α-manganese and in β-manganese.

In many metals each atom is attached to some of its neighbors by strong bonds and to others by much weaker bonds. An extreme case is β-tungsten, in which there are straight strings of strongly bonded atoms. Similar strings are also present in the α-uranium structure.

The use of the radii is illustrated by the discussion of two compounds, cementite and AuSn.

PASADENA, CALIFORNIA RECEIVED SEPTEMBER 28, 1946

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1100]

Some Spectroscopic Changes Connected with the Stereoisomerization of Diphenylbutadiene

BY A. SANDOVAL AND L. ZECHMEISTER

In the present study we wished to investigate how far some methods used and conclusions drawn in the field of *cis-trans* isomeric carotenoids[1] find their parallels in the structurally simpler case of diphenylbutadiene. As shown by Fig. 1, this stereoisomeric set includes only three members, the two *cis* forms of which represent sterically "hindered" isomers because two hydrogen atoms, one belonging to the nucleus and the other to the open chain, constitute a spatial conflict.[2] Since, however, as in the case of stilbene, these hindered *cis* forms are without competition by non-hindered ones, they may appear in substantial quantities under favorable conditions when all-*trans*-diphenylbutadiene undergoes a spatial change.

Although Kuhn and Winterstein[3] by their synthetic methods obtained exclusively the ordinary, all-*trans* form of diphenylbutadiene, Straus[4] had shown earlier in his remarkable contribution that by the reduction of diphenyldiacetylene the *cis-cis* form, m. p. 70–70.5°, can be prepared and by the hydrogenation of diphenylbutenine, the third, oily *cis-trans* isomer.

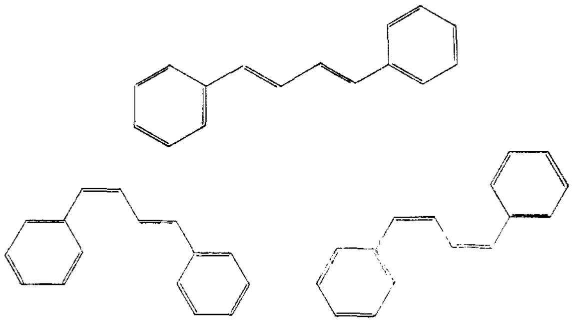

Fig. 1.—*trans-trans*-, *cis-trans*, and *cis-cis*-diphenylbutadienes (values used: C=C, 1.33 Å.; C—C, 1.46 Å.; and C=C—C angle, 124° 20′).

It has been reported that upon the addition of catalytic quantities of iodine, in light, for example, to a hexane solution of β-carotene, the height of the maximum extinction decreases very considerably, *viz.*, by about 20%. We observed that the corresponding decrease in the case of diphenylbutadiene is less marked and amounts only to 3.5%, and that no noticeable change in the wave length occurs (Fig. 2).

While preparative quantities of diphenylbutadiene can be handled without apparent stereoisomerization, a conspicuous *trans* → *cis* shift takes place if a solution with a concentration as low as a few micrograms per milliliter is kept for half to one hour in diffuse daylight. As shown in Figs. 2 and 3 (dash-circle lines), the fine structure of the

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(1) General survey: L. Zechmeister, *Chem. Rev.*, **34**, 267 (1944).

(2) L. Zechmeister and A. L. LeRosen, THIS JOURNAL, **64**, 2755 (1942).

(3) R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 87 (1928).

(4) F. Straus, *Ann.*, **342**, 190 (1905); confirmed and partly extended by C. Kelber and A. Schwarz, *Ber.*, **45**, 1946 (1912), as well as by E. Ott and R. Schröter, *Ber.*, **60**, 624 (1927). One of the present authors (ref. 1, p. 339) tentatively assigned a *cis-cis* configuration to the oily form; however, on the basis of recent experiments it seems now that Straus' original interpretation is more probable.

fundamental band practically disappears and, simultaneously, the height of the main maximum decreases to 55 and 60% of the original value, in hexane and benzene solutions, respectively. It can easily be proved that photochemical destruction is not responsible for this effect: Upon iodine catalysis, in light, the initial fine structure reappears and the extinction curve becomes identical with that which iodine produces from the pure all-*trans* compound (dash-dot lines).

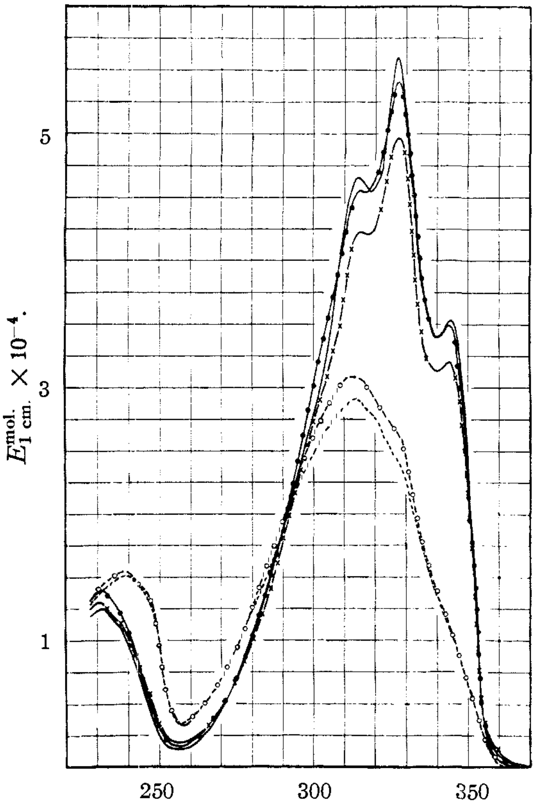

Fig. 2.—Molecular extinction curves of diphenylbutadiene, in hexane: ———, fresh solution of the all-*trans* compound; —o—o—, after thirty minutes of standing in scattered daylight; —●—●—, obtained upon iodine catalysis of either of the foregoing solutions; — — —, after six minutes insolation of fresh all-*trans* solution; —x—x—, catalyzed with iodine after six minutes insolation.

Similar spectroscopic effects appear when very dilute all-*trans*-diphenylbutadiene solutions are exposed to sunshine ("insolation"). However, this *trans* → *cis* change, which required six to seven minutes under the conditions applied, was accompanied by moderate destruction. The extinction values at 328 mμ were found, upon iodine catalysis, to be 8% lower than the corresponding value of $\lambda_{\text{max.}}$ value when diffuse light was used as mentioned in hexane (Fig. 2; *cf.* Fig. 3).

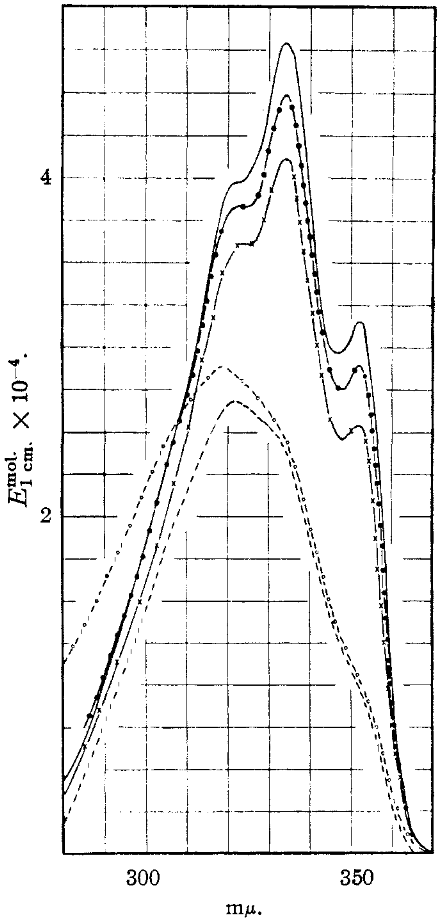

Fig. 3.—Molecular extinction curves of diphenylbutadiene, in benzene; ———, fresh solution of the all-*trans* compound; —o—o—, after thirty minutes standing in scattered daylight, —●—●—, upon iodine catalysis of either of the foregoing solutions; — — —, after six minutes insolation of fresh all-*trans* solution; —x—x—, catalyzed with iodine after six minutes insolation.

It is convenient to follow the gradual change of all-*trans*-diphenylbutadiene during photo-isomerization by means of illumination from a suitable electric bulb (Experimental). As shown by Fig. 4, the initial maxima in benzene, located at 352 and 334 mμ, decrease and then disappear while the small original plateau at 320 mμ becomes a new main maximum which is, however, devoid of fine structure. Further illumination during a reasonably long period of time produced no additional change in the curve. It can be proved by iodine catalysis of the illuminated solution that practically no photochemical destruction has taken place (Fig. 4).

These spectroscopic observations were confirmed by chromatographic experiments. If a solution of 100 mg. of ordinary diphenylbutadiene in 100 ml. of petroleum ether is developed on alumina with the same solvent, a slow migration but no differentiation of the intensely fluorescing zone takes place. In contrast, when a similar solution is chromatographed after the exposure to a strong

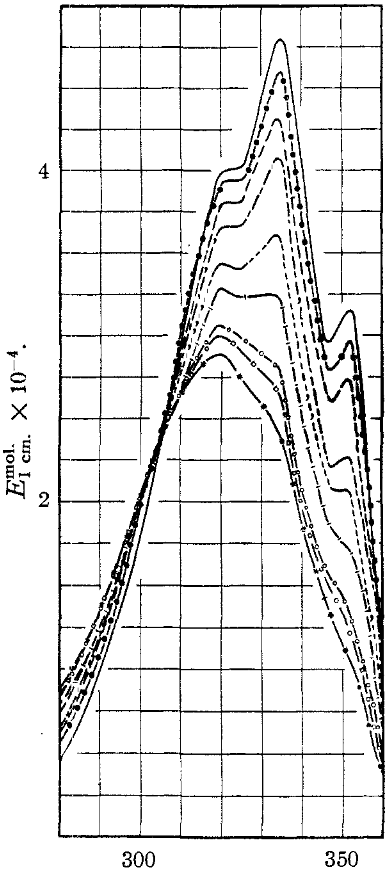

Fig. 4.—Molecular extinction curves of diphenylbutadiene in benzene. Gradual disappearance of fine structure in the course of illumination with a 200-watt Mazda bulb from 10-cm. distance, with cooling: ———, fresh solution of the all-*trans* compounds; — —, after 5 min.; – – –, 10 min.; - - - - -, 20 min.; —1—1—, 30 min.; —o—o—, 40 min.; —□—□—, 50 min.; and —*—*—, 390 min. illumination; and —●—●—, upon iodine catalysis at the end of 390 min. illumination.

artificial light source for twenty-four hours, a second zone, which contains four-fifths of the material, appears below the unchanged portion of the all-*trans* form. This *cis* zone does not fluoresce but can be located because it quenches the slight fluorescence of the adsorbent in strong ultraviolet light.

The molecular extinction curve (Fig. 5, dashed line) of the *cis* compound contained in the new zone shows a lower value at $\lambda_{max.}$ than non-chromatographed stereoisomeric mixtures obtained by illumination. Furthermore, the disappearance of the last traces of the initial fine structure in the fundamental band confirms the absence of the all-*trans* form. Again, iodine catalysis proved that practically only reversible spatial changes occurred during the experiment (Fig. 5).

In order to facilitate the diagnosis of mixtures of stereoisomeric diphenylbutadienes, we give

TABLE I

MOLECULAR EXTINCTION COEFFICIENTS OF STEREOISOMERIC DIPHENYLBUTADIENES AT THE MAXIMA (*italicized*) AND MINIMA

All-*trans* form		Chromatographically homogeneous *cis* form		Mixture of stereoisomers obtained upon iodine catalysis	
mμ	$E^{mol.}_{1\ cm.} \times 10^{-4}$	mμ	$E^{mol.}_{1\ cm.} \times 10^{-4}$	mμ	$E^{mol.}_{1\ cm.} \times 10^{-4}$
		In hexane			
344	*3.53*			*344*	*3.49*
340	3.41			340	3.40
328	*5.61*			*328*	*5.40*
318	4.58			317	4.53
314–315	*4.65*	*313*	*3.04*	*315–316*	*4.55*
256–257	0.15	256	0.36	255	0.16
230–231	*1.26*	*238–240*	*1.72*	*230–231*	*1.39*
		In benzene			
352	*3.15*			*352*	*2.89*
348	2.98			348	2.76
334	*4.79*	*319–320*	*2.61*	*334*	*4.49*

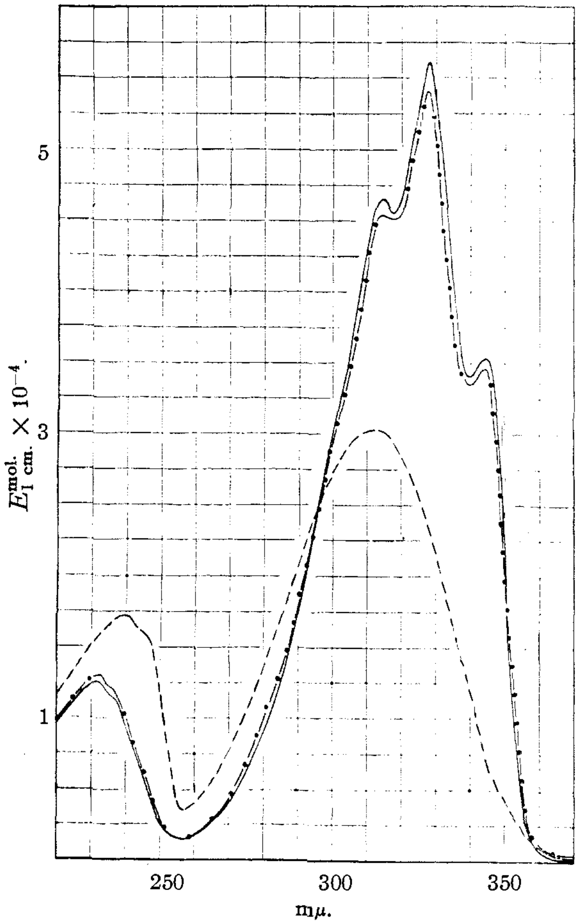

Fig. 5.—Molecular extinction curves of diphenylbutadiene in hexane: ———, fresh solution of the all-*trans* compound; — — —, chromatographically separated *cis* compound; and —●—●—, upon iodine catalysis of the *cis* compound.

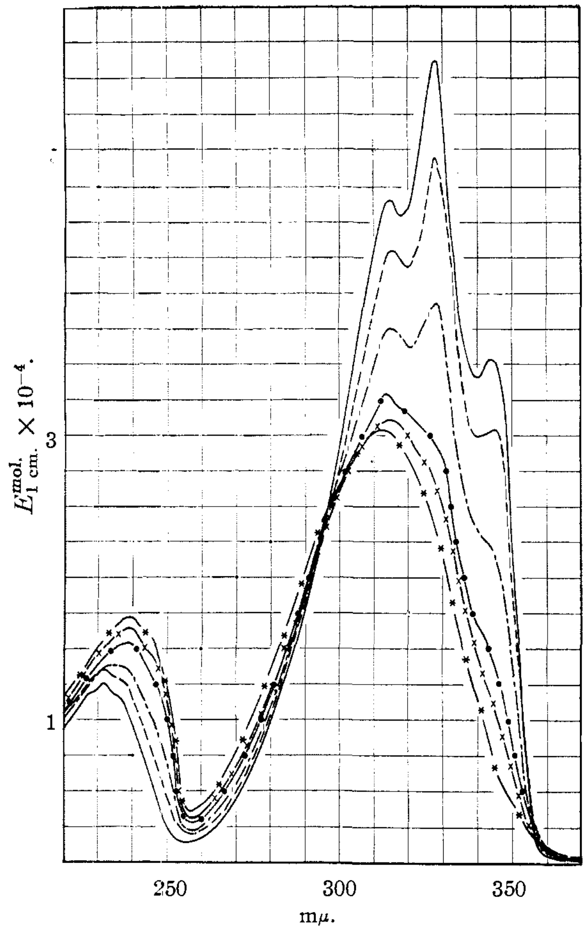

Fig. 6.—Molecular extinction curves of diphenylbutadiene in hexane. Artificial mixtures of chromatographically homogeneous *trans* and *cis* forms. The following figures indicate % *cis* compound contained in the respective mixtures: ———, 0%; — —, 20%; — — — —, 50%; —●—●—, 80%; —x—x—, 90%; and —*—*—, 100%.

Fig. 6 in which the extinction curves of some artificial mixtures are reproduced; the latter were prepared from chromatographically homogeneous substances.

The photochemical behavior of the *cis* isomer contained in the bottom zone of chromatograms is illustrated in Fig. 7. When isolated, this substance forms an oil; no crystals with m. p. 70° as prepared by earlier authors[4] could be obtained by irradiation so far. When the oily isomer was illuminated with an electric bulb, crystals began to appear within a minute, and the starting material had almost completely disappeared within an hour. Upon recrystallization, the product showed a melting point of 150°, a strong fluorescence in ultraviolet light and the typical forms of the all-*trans*-diphenylbutadiene platelets (Fig. 8).

Very dilute solutions of our oil did not show any spectroscopic shifts when kept in the diffuse daylight of the laboratory for several days, nor did the oil change when stored in darkness.

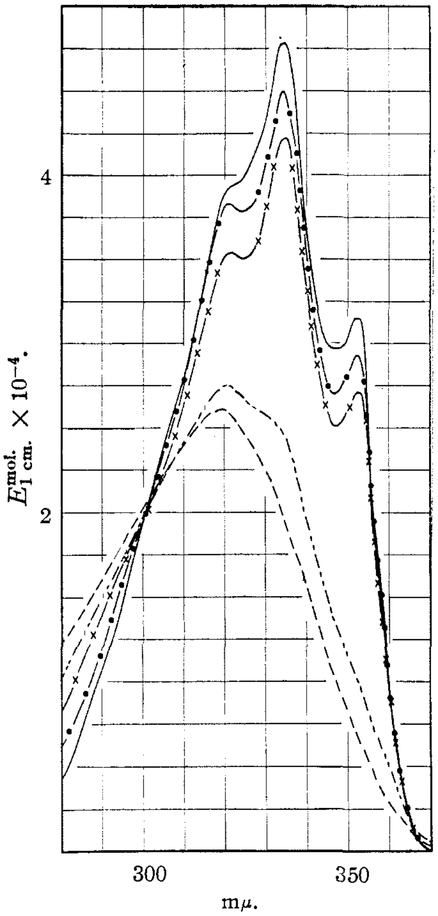

Fig. 7.—Molecular extinction coefficient of diphenylbutadiene in benzene. Behavior of the chromatographically homogeneous *cis* form when illuminated with a 200-watt lamp as in Fig. 3. — — —, before illumination; — — — —, after 5 min.; and —x—x—, ninety minutes illumination; —●—●—, upon iodine catalysis at the end of ninety minutes illumination; ——— fresh solution of the all-*trans* form (in order to compare with the curve of the iodine catalyzed mixture of stereoisomers).

We intend to correlate, if possible, the described phenomena with some preparative findings of earlier authors. The present study is also being extended to other synthetic polyenes.

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

Experimental

Adsorbents and Solvents.—As adsorbent, commercial alumina Alorco, Grade A (−200 mesh) was used or, when this brand was not obtainable, the Grade F (−80 mesh) was ground to −200 mesh. Both materials should be mixed with 20–25% celite. The "petroleum ether" was Skellysolve B, b. p. 60–70°, and the "light petroleum ether," Skellysolve A, b. p. 28–38°.

All-*trans*-diphenylbutadiene was synthesized from phenylacetic acid and cinnamaldehyde.[3] Since the end product obtained was slightly yellowish, we purified it further, by developing 1-g. portions in 250 ml. of petroleum ether on 36 × 5.2 cm. alumina columns, with 1 liter of the same solvent containing 3% acetone. The main, bluish fluorescing zone, 15-mm. broad, reached the bottom section while yellowish fluorescing contaminants remained near the top. The diphenylbutadiene was cut out, eluted with acetone, transferred into petroleum ether with water, dried with sodium sulfate and completely evaporated *in vacuo*. These operations should be carried out in darkness. After recrystallization from ethanol, the sample was white and showed the m. p. 152–153° (cor., Berl block).

Anal. Calcd. for $C_{16}H_{14}$: C, 93.37; H, 6.63. Found: C, 93.35; H, 7.04.

The fluorescence of adsorbates increases when the solvent evaporates from the surface of the extruded column. The fluorescence in hexane solution is blue, and in benzene bluish violet which can be observed even in diffuse daylight. No marked fluorescence appeared in dilute methanol or acetone solutions. Refluxing in darkness for an hour did not alter the extinction curve (Fig. 2). Petroleum ether solutions of our samples do not give a coloration on filtrol.

Light Sources and Conditions of Illumination.—All solutions were exposed in ordinary volumetric flasks. In insolation experiments the concentration was 3μg./ml., and the end temperature 28 to 42°. By "scattered daylight" we mean the light reaching the solution (placed on the window sill), without direct sunshine, through the laboratory windows, on a sky-blue day in the early afternoon hours.

For the purpose of artificial illumination, when the total amount of the diene did not exceed a milligram, a regular 200-watt General Electric Mazda bulb was used (frosted, tungsten filament, distance from glass to glass, 10 cm.). The flask was cooled with a film of running water. For 100–150 mg. samples a Mazda clear projection lamp, 250-watt, is recommended (distance, 3.5 cm. from the center of the lamp to the wall of the flask). This lamp was encased in a water jacket and the flasks surrounding it were cooled by an air stream.

For the purpose of catalytic experiments, iodine (5% of the weight of the diphenylbutadiene) was added to the solution which was then illuminated for ten to twenty minutes with a 3500° Mazda white fluorescent lamp (distance, 60 cm.; length of the tubes, 120 cm.). An extension of the illumination period to an hour proved to be without influence. The same light source is scarcely effective in the absence of iodine.

For the inspection of chromatograms and extruded columns the portable ultraviolet lamp, "Mineralight Q31," was used which was equipped with two dark-violet light filters (Ultraviolet Products, Inc., Santa Monica, California). Some ultraviolet bulbs were unsuitable for the present purpose.

The extinction curves were taken in a Beckman photoelectric spectrophotometer.

Small-scale Experiments in Sunshine.—The figures listed in Table II refer to a petroleum ether solution. They demonstrate how the steric changes are increasingly complicated during the insolation by irreversible destruction processes which, finally, take the upper hand.

TABLE II

EXPOSURE OF DIPHENYLBUTADIENE (IN PETROLEUM ETHER) TO SUNSHINE

Time of insolation, min.	0	1/3	2/3	1	5	6	35	80
Extinction at 328 mμ, after iodine catalysis, %	100	100	98	95	91	87	71	33

Under these conditions the *trans* → *cis* rotation occurred at a high speed. After only one-third minute of exposure the fine structure was lost and the spectral curve was very similar to that in Figs. 2 and 3 (dash–circle), except for a slight plateau between 320 and 328 mμ. The only marked change during further insolation, up to seven minutes, was the disappearance of this plateau. The iodine catalysis test did not indicate any considerable destruction at this point. Evidently, the optimum conditions for achieving the desired steric change lay between five and seven minutes under the conditions applied.

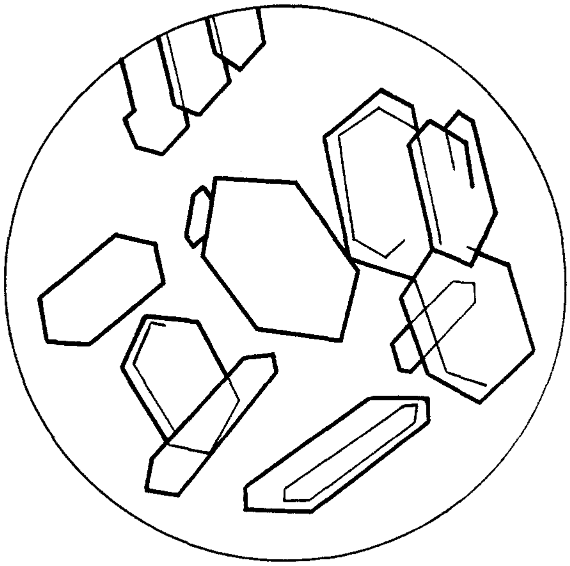

Fig. 8.—Crystals of ordinary (all-*trans*-) diphenylbutadiene, from ethanol. Identical forms were observed upon illumination of the oily *cis* form and subsequent recrystallization.

***trans* → *cis* Photoisomerization of Diphenylbutadiene on a Preparative Scale.**—Six 75-mg. portions, each dissolved in 100 ml. of petroleum ether, in volumetric flasks, were exposed to the projection lamp mentioned for twenty-four hours and the combined solutions were evaporated *in vacuo*, in darkness. The partially crystalline, oily residue was dissolved in a few ml. of petroleum ether and developed with 1.5 liters of the same solvent on a 25 × 4.1 cm. alumina column (the figures on the left denote width of the zones, in mm.; "fl" = fluorescence)

1	intensely blue fl.; contaminant
2	narrow streaks, yellow fl.; contaminants
25	empty interzone
28	blue fl.: unchanged all-*trans* form
22	empty interzone
110	no fl., alumina darker than elsewhere: *cis*-form
62	empty section

The interzones showed a slight fluorescence of the adsorbent in "Mineralight."

Both zones were eluted with acetone and transferred into light petroleum ether. As established by iodine catalysis, the weight ratio of the isomers contained in the two zones was unchanged all-*trans*:*cis* = 16:84. In a second chromatogram traces of all-*trans*-butadiene could be eliminated from the *cis* form. The behavior of the latter was studied in 50–100-mg. portions which were sealed in evacuated glass tubes. Heating to 100° in darkness for ninety minutes did not alter the extinction curve. The conversion into the crystalline *trans* form was achieved by illuminating with the 200-watt lamp (see above and Fig. 8).

Summary

The *cis–trans* isomerization of diphenylbutadiene, $C_6H_5(CH{=}CH)_2C_6H_5$, was studied by some spectroscopic and chromatographic methods.

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