[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

Geometric Isomers of 1-Phenyl-1,3-butadiene[1]

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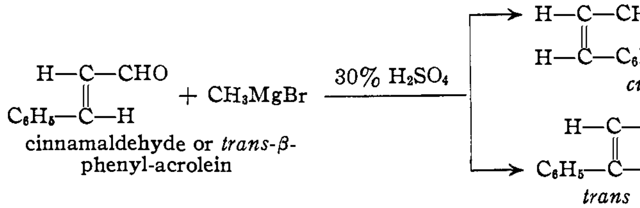
Contrary to previous reports, only *trans*-1-phenyl-1,3-butadiene can be obtained by the acid hydrolysis of cinnamaldehyde-methylmagnesium bromide. The new *cis* isomer has been made by photochemical isomerization of the *trans*, a reaction which appears to be reversible. For each isomer in about 99% purity there is given the distilling range, freezing point, refractive index, density, ultraviolet and infrared absorption spectra. The *trans* compound reacts quantitatively in a Diels–Alder reaction with maleic anhydride under conditions where the *cis* does not react. Neither isomer forms a cyclic or polymeric sulfone. Polymerization appears to give mostly dimer in the case of the *trans*. Some differences in properties may be the result of steric inhibition of resonance in the *cis*.

This study was undertaken (1) to determine the amounts of *cis*- and *trans*-1-phenyl-1,3-butadienes produced by the cinnamaldehyde–methylmagnesium bromide synthesis[3a,b]



(2) to obtain each isomer in pure form by varying the conditions of hydrolysis in this reaction according to an earlier report,[4] and (3) to observe certain physical and chemical properties of the isomers.

Fractional distillation of this phenylbutadiene gave no indication of a mixture of isomers. The preferential Diels–Alder reaction with maleic anhydride, which has been applied successfully to the piperylenes,[5,6] depends on the greater reactivity of the *trans* isomer because of the steric hindrance in the *cis* form by the terminal methyl group to 1,4-addition of maleic anhydride.[7] A modified determination of the maleic anhydride value[8] of this phenylbutadiene showed that 98–99% of the theoretical amount of anhydride reacted at 110° to form only 3-phenyl-Δ^4-*cis*-tetrahydrophthalic anhydride.[9]

When phenylbutadiene was allowed to react with less than the theoretical quantity of maleic anhydride at room temperature (to minimize isomerization and polymerization) and the unreacted diene recovered, its density, refractive index, and ultraviolet absorption spectrum did not differ significantly from the original hydrocarbon (Table I). This result and the substantially quantitative reaction with maleic anhydride prove that only the *trans* isomer is formed from cinnamaldehyde and methylmagnesium bromide under the conditions described.[3a,b,10]

By analogy with the piperylenes this *trans*-phenylbutadiene should add sulfur dioxide to form the monomeric cyclic sulfone which, on thermal dissociation, should regenerate the *trans* isomer.[6] Attempts to prepare a cyclic *trans*-phenylbutadiene sulfone or a polymeric sulfone were unsuccessful (Tables VI and VII). This surprising lack of reactivity has been investigated in the case of related terminally substituted butadienes.[11]

According to Muskat and Herrman,[4] hydrolysis of the cinnamaldehyde–methylmagnesium bromide adduct in 30% sulfuric acid without stirring or cooling yields *cis*-phenylbutadiene, while hydrolysis in cold 50% sulfuric acid gives the *trans*. Several careful repetitions of these experiments showed that both reactions gave impure products which yielded the *trans* isomer only after purification.[12] The purified products reacted with maleic anhydride to give phenyl tetrahydrophthalic anhydride[9] and showed ultraviolet absorption curves *identical* with the authentic *trans* isomer (Fig. 1).

Since it appeared that pure *cis*-phenylbutadiene had not been made,[13] its preparation was undertaken by photochemical isomerization of the *trans* isomer. Samples prepared in the dark and under ordinary laboratory illumination were identical but exposure to sunshine in Pyrex or quartz markedly altered the ultraviolet absorption. A shift in absorption maximum from 280 to 270 mμ was accompanied by a decrease in specific extinction. The pure *cis* isomer was obtained by

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[1] First reported in a Communication to the Editor, THIS JOURNAL, **71**, 4157 (1949). Presented before the Division of Organic Chemistry at the Philadelphia meeting of the American Chemical Society, April 10, 1950.

[2] du Pont fellow, 1948–1949.

[3] (a) Grummitt and Becker, THIS JOURNAL, **70**, 149 (1948); (b) *Org. Syntheses*, **30**, 75 (1950).

[4] Muskat and Herrman, *ibid.*, **53**, 252, 260 (1931); **54**, 2001 (1932).

[5] Robey, Morrell and Wiese, *ibid.*, **63**, 627 (1941).

[6] Craig, *ibid.*, **65**, 1006 (1943).

[7] This stereochemical selectivity has been observed for other dienophiles and for other dienes. For example, *trans*-piperylene with acrolein gives a 56% yield while the *cis* isomer does not react (ref. (14) and Petrov, *Zhur. Obschchei Khim.*, (*J. Gen. Chem.*), **18**, 1125 (1948); *C. A.*, **43**, 1731 (1949)). Only one of the two isomeric 1-cyano-1,3-butadienes reacts with maleic anhydride; this was assigned the *trans* configuration (Snyder, Stewart and Myers, THIS JOURNAL, **71**, 1055 (1949)).

[8] Ellis and Jones, *Analyst*, **61**, 812 (1936).

[9] Diels, Alder and Pries, *Ber.*, **62B**, 2081 (1929).

[10] Recently, Alder, Vagt and Vogt, *Ann.*, **565**, 135 (1949), also observed that only *trans*-phenylbutadiene was obtained from cinnamaldehyde *via* methylstyrylcarbinol and methylstyrylcarbinyl chloride, a synthesis described earlier by Klages, *Ber.*, **35**, 2649 (1902).

[11] Grummitt and Splitter, Organic Division, American Chemical Society Meeting in Chicago, Ill., Sept. 5, 1950.

[12] Braude, Jones and Stern, *J. Chem. Soc.*, 1087 (1947), reported that the low refractive indices given in reference (4) were probably due to considerable amounts of methylstyrylcarbinol and polymerized phenylbutadiene.

[13] As this paper was being written, Voronkov, Broun, Karpenko and Gol'shtein, *Zhur. Obshchei Khim.* (*J. Gen. Chem.*), **19**, 1356 (1949) and *C. A.*, **44**, 1955 (1950), reported that an iodine-catalyzed dehydration of methylstyrylcarbinol and distillation of the product had given two isomers: the *trans*, b.p. 69.2° at 4 mm., n^{20}_D 1.60852, d^{20}_4 0.9338; the *cis*, b.p. 76.9° at 3 mm., n^{22}_D 1.60948, d^{20}_4 0.9334. These properties differ from our data (Table II); the order of the boiling points is reversed, and these isomers are very close in index and density. The index and density suggest that both consist largely of the *trans* isomer.

TABLE I

PHYSICAL PROPERTIES OF *trans*-1-PHENYL-1,3-BUTADIENE BEFORE AND AFTER MALEIC ANHYDRIDE TREATMENT

Sample	Dist. temp. °C.	Mm.	$n^{25}\text{D}$	d^{25}_4	U. V. absorption, sp. ext., 280 mμ[a]
Original	65–66.5	3.5	1.6079	0.9254	227
Treated	78–79	11	1.6083	.9251	227

[a] Determined with ethanol solutions. The spectral curves plotted over the range of 220 to 300 mμ were identical. The curve for the *trans* isomer is shown in Fig. 1.

irradiating with ultraviolet lamps a 5% ethanol solution of the *trans* isomer in Pyrex at 36° for several days and treating the product with maleic anhydride to extract the unconverted *trans* compound. Traces of methylstyrylcarbinol were removed with solid methylmagnesium bromide and the product repeatedly treated with activated alumina until the refractive index and density remained unchanged. Physical properties of *cis* and *trans*-phenylbutadiene are given in Table II, the ultraviolet absorption curves in Fig. 1, and the infrared absorption curves in Figs. 3 and 4.

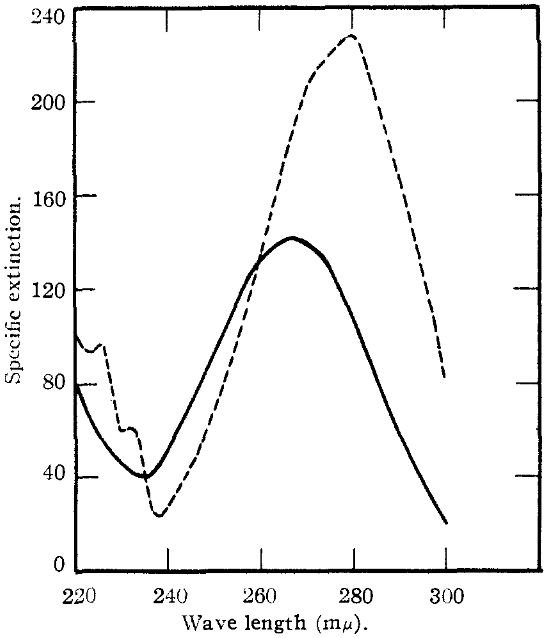

Fig. 1.—Ultraviolet absorption spectra of *cis*-1-phenyl-1,3-butadiene (solid line) and of *trans*-1-phenyl-1,3-butadiene (broken line).

TABLE II

PHYSICAL PROPERTIES OF *cis*- AND *trans*-1-PHENYL-1,3-BUTADIENE

	cis	*trans*
Dist. temp., °C.	71 (11 mm.)	83 (11 mm.)
Freezing point, °C.	−56.99 ± 0.04	4.52 ± 0.04
$n^{25}\text{D}$	1.5822	1.6089
d^{25}_4	0.9197	0.9232
Molar ref.[a]	47.25	48.82

[a] Calculated by the Lorentz-Lorenz equation, 43.85.

The *cis* isomer is also photochemically isomerized, as the curves in Fig. 2 show, probably forming an equilibrium *cis–trans* mixture along with some polymer. A comparison of these curves with that of the pure *cis* compound (Fig. 1) suggests that the *cis* isomer predominates in these mixtures.

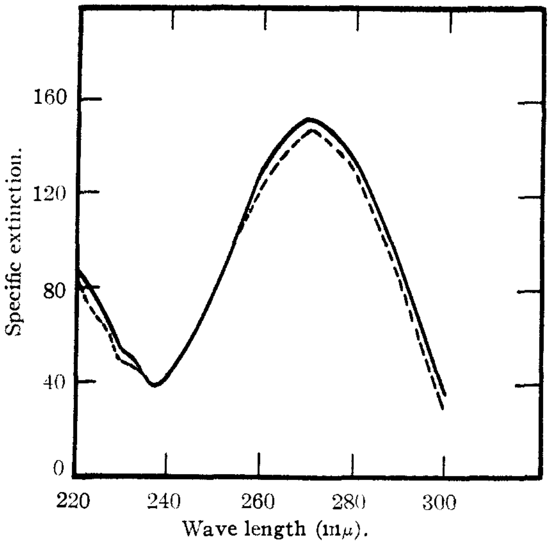

Fig. 2.—Ultraviolet absorption spectra of *cis*-phenylbutadiene (solid line) and *trans*-phenylbutadiene (broken line) after 4 hr. exposure to sunlight.

An iodine-catalyzed reaction with the *trans* isomer, which has been reported to isomerize both *cis*- and *trans*-piperylenes to an equilibrium mixture,[14] did not yield *cis*-phenylbutadiene, as determined by ultraviolet absorption spectra (*cf.* reference (13)). It is noteworthy that irradiation failed to isomerize the piperylenes.[14]

cis-1-Phenyl-1,3-butadiene does not react with maleic anhydride at room temperature within four days. In refluxing toluene solution for four hours about 5% of the theoretical quantity of anhydride reacted, as compared with 98–99% for the *trans* isomer. With sulfur dioxide the *cis* compound failed to form either a monomeric or polymeric sulfone. Both isomers added bromine readily to give identical tetrabromide derivatives.

The phenylbutadienes differ in their polymerization behavior. At room temperature the *trans* isomer forms phenylbutadiene dimer mostly, as shown by the *decrease* in refractive index (Table III).[15]

TABLE III

UNCATALYZED POLYMERIZATION OF *trans*-PHENYLBUTADIENE AT ROOM TEMPERATURE (EXPT. 3)[a]

Physical prop.	Time Zero	50 days
$n^{25}\text{D}$	1.6087	1.6062
d^{25}_4	0.9234	0.9875
Visc. (25°), poises	0.0136	0.2965
U. V. absorption, sp. extinction at 284 mμ in chloroform[b]	224	117

[a] The freshly distilled hydrocarbon was allowed to stand in a nitrogen filled bottle. [b] In chloroform the maximum is at 284 mμ; in ethanol, at 280 mμ (Fig. 1).

The formation of phenylbutadiene polymer in the attempts to make sulfones from the *trans* compound

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(14) Frank, Emmick and Johnson, THIS JOURNAL, **69**, 2313 (1947).

(15) Liebermann and Riiber, *Ber.*, **35**, 2696 (1902); Stobbe and Reuss, *ibid.*, **45**, 3496 (1912).

indicated that sulfur dioxide catalyzes polymerization. This was verified by the experiments summarized in Table IV. As the refractive indexes show, there is dimer formation initially and then polymerization.

TABLE IV

SULFUR DIOXIDE-CATALYZED POLYMERIZATION OF *trans*-PHENYLBUTADIENE AT ROOM TEMPERATURE

Expt.	Method	Time	n^{25}D	n^{25}D of blank[a]
1	Sample + liq. SO_2 in a sealed tube	0	1.6092	
		18 hr.	1.6008	
		66	1.6108	
		90	solid	
2	SO_2 bubbled in	0	1.6069	1.6069
		1 day	1.6060	1.6069
		3	1.6052	1.6068
		11	1.6088	1.6067
		14	1.6144	1.6067
		25	1.6210	1.6064
		50	solid	1.6061

[a] Purified nitrogen was bubbled through a second sample in the same way that sulfur dioxide was used.

The *cis* compound at 0° polymerizes slowly: after one month the refractive index had increased 0.0008, and the density, 0.0051. When each isomer was heated at 79.7° for 15 days, the increasing refractive index of the *cis* indicated polymerization, while the decrease to a constant value for the *trans* was the result of dimerization (Table V). Similar differences in polymerization behavior have been reported for the isomeric piperylenes.[14]

TABLE V

THERMAL POLYMERIZATION OF *cis*- AND *trans*-1-PHENYL-1,3-BUTADIENE AT 79.7 ± 0.1°

Time, hr.	Refractive index, 25° *cis*	Refractive index, 25° *trans*
0	1.5822	1.6089
20	1.5841	1.6069
67	1.5932	1.6057
118	1.6002	1.6054
357	1.6114	1.6057

Experimental

***trans*-1-Phenyl-1,3-butadiene.**—Repeated vacuum distillations and a fractional vacuum distillation through a 12-plate glass helix-packed column of the cinnamaldehyde-methylmagnesium bromide product[3a,b] showed that it was homogeneous. The second and third distillates at 55° (2 mm.) showed n^{25}D of 1.6080 and 1.6081, respectively. A subsequent fractional distillation through the column gave:

Fraction, ml.	n^{25}D	d^{25}_4
3.8	1.6080	0.9256
7.0	1.6083	.9249
7.0	1.6087	.9245
4.5	1.6082	.9245

The low index and high density of the first fraction are probably due to methylstyrylcarbinol, n^{20}D 1.5692 and $d^{27.4}_4$ 1.040.[16]

The most highly purified material was made by allowing 85.6 g. of the once-distilled phenylbutadiene and 1.1 g. of solid methylmagnesium bromide (made by vacuum distilling ether from a Grignard solution) to stand one day and then distilling at room temperature and approximately 0.1 mm. in a Hickman pot still. The distillate was frozen in an ice-bath, allowed to melt partly, and the liquid portion removed by suction. This operation was repeated five times with the removal of 2–4 ml. of liquid in each step. A final vacuum distillation at 0.1 mm. gave 50.6 g. Figures 1 and 4 and Table II show the physical properties of this sample.

***trans*-1-Phenyl-1,3-butadiene Plus Maleic Anhydride.**—This reaction was carried out in two different ways. A quantitative measure of the maleic anhydride consumed was made by a modification of the Ellis and Jones diene analysis.[8] Duplicate 1-g. samples of the hydrocarbon weighed to three places were diluted with 25 ml. of redistilled reagent toluene, 25 ml. of a maleic anhydride–toluene solution containing about 1.6 g. of anhydride was pipetted into each sample, and the solutions, along with two blanks, were refluxed in all-glass apparatus for 4 hours. After adding 5 ml. of water and refluxing for 20 minutes, the condenser was washed down with 5 ml. of pure ether and 20 ml. of water, the solution was transferred to a 250-ml. separating funnel with water and ether to rinse the flask. After separating the aqueous layer, washing the toluene solution with 25- and 10-ml. portions of water, the combined water solutions were titrated with 1.0 *N* sodium hydroxide solution. From the difference in alkali equivalents between the blanks and the samples, the quantity of anhydride consumed was calculated. For duplicate samples of *trans*-phenylbutadiene 98.8 and 98.3% of the theoretical quantity of anhydride reacted. The addition compound recovered from the toluene solution melted 118.5–120.0° after one crystallization from benzene.[9]

At room temperature (28–32°) instead of 110° (boiling toluene), the consumption of anhydride in 3.5 hours is 30%; in 9.0 hours, 58%; and in 18.0 hours, 71%.

The second reaction with maleic anhydride also showed the homogeneity of the phenylbutadiene. The reaction was run at room temperature to minimize isomerization and polymerization with excess hydrocarbon, recovering the hydrocarbon and comparing its physical properties with those of the original sample. A mixture of 15.0 g. (0.115 mole) of phenylbutadiene and 0.075 g. of phenyl-β-naphthylamine dissolved in 30 ml. of toluene and 5.621 g. (0.575 mole) of maleic anhydride dissolved in 60 ml. of toluene was allowed to stand at room temperature for 4 days. Addition of water and titration showed that 0.048 g. of anhydride remained and therefore 49.3% of the phenylbutadiene had reacted. The unreacted hydrocarbon was recovered from the toluene solution by vacuum distillation. Table I summarized the physical properties of the original and treated phenylbutadienes.

***cis* and *trans*-Phenylbutadienes (Muskat and Herrman).**[4]—Our interpretation of these procedures was as follows: the "*cis*" isomer was made by taking one-half of the Grignard adduct obtained from 100 g. (0.76 mole) of redistilled cinnamaldehyde, 250 g. of 4 *M* methylmagnesium bromide (Arapahoe Chemical Co.) and 500 ml. of absolute ether, which reacted at 0–10°, and pouring it slowly into 1 l. of 30% sulfuric acid without stirring or cooling. After standing overnight the ether layer was separated, washed with water, dried over potassium carbonate, and distilled. Contrary to the earlier report, no constant boiling fraction was obtained up to 130° at 3 mm. Therefore, this distillate was further dried with barium oxide, 0.1% of phenyl-β-naphthylamine added, and redistilled at 1 mm.: 2.4 g. at 53–63°, n^{25}D 1.5993; 3.0 g. at 83–96°, n^{25}D 1.5828; 5.9 g. residue, n^{25}D 1.5789. The first two fractions were combined and distilled twice from about 1 g. of solid methylmagnesium bromide in a Hickman still at 27° (0.15 mm.); the final distillate showed n^{25}D 1.6054. The ultraviolet absorption curve was identical with the pure *trans* of Fig. 1. The maleic anhydride adduct after one crystallization from benzene melted 118.6–120.2° and showed no depression in a mixed melting point with adduct from the authentic *trans* isomer.

The *trans* isomer was obtained from the remainder of the Grignard adduct by adding it with stirring to 620 ml. of 50% sulfuric acid during one hour and holding the temperature at 6°. The ether layer was washed with water, dilute ammonium hydroxide, water, dried over potassium carbonate, and distilled up to 105° (2 mm.) but no constant boiling fraction, as described,[4] was obtained. After redrying over barium oxide and redistilling at 2 mm., there was obtained at 61–64°, 9.3 g., n^{25}D 1.6092; at 70–76°, 1.0 g., n^{25}D 1.6059; and 1.7 g. of residue. Purification of the first fraction with Grignard agent and distillation at 27° (0.15 mm.) gave 4.8 g., n^{25}D 1.6078. The ultraviolet absorption curve was identical with the pure *trans* of Fig. 1. The crystallized maleic anhydride adduct melted 118.4–120.0° and

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(6) Kenyon, Partridge and Phillips, *J. Chem. Soc.*, 85 (1936).

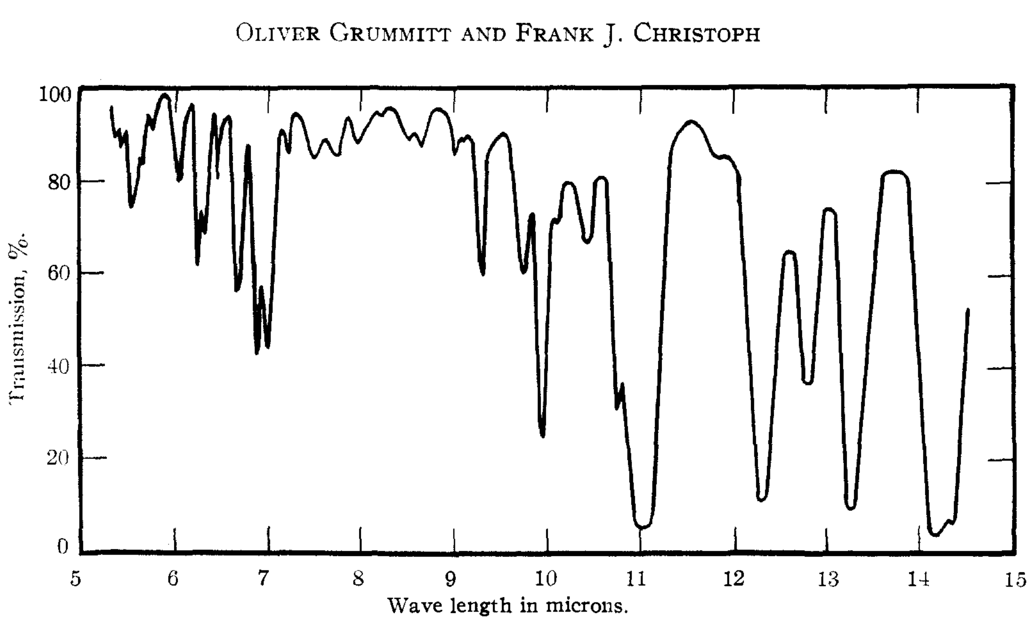

Fig. 3.—Infrared absorption spectrum of *cis*-phenylbutadiene.

showed no depression in a mixed melting point with the adduct from the pure *trans* isomer.

It was also reported that the "*cis*" isomer isomerized on treatment with hydrochloric acid–calcium chloride followed by distillation to the *trans* form.[4] Since the "*cis*" is actually the *trans* isomer, this isomerization was tried on the *trans* isomer made in our work. The boiling point and refractive index 64.5–66° (3 mm.) and n^{25}D 1.6084, were unchanged.

***trans*-Phenylbutadiene Plus Sulfur Dioxide.**—Experiments 1–5 (Table VI) for the preparation of the cyclic sulfone were carried out in pressure bottles. Phenyl-β-naphthylamine (1%) was used as a polymerization inhibitor. After the reaction the sulfur dioxide was allowed to escape, the residue was extracted with two 30-ml. portions of hot (60°) water and then with 60 ml. of hot (60°) 50% ethanol. Evaporation of the extracts under vacuum left no residue. A qualitative sulfur test (sodium-fusion) on the water-insoluble, ether-soluble viscous-portion was negative. This residue may contain free phenylbutadiene, as well as polymerized phenylbutadiene; in Expt. 5 the residue with maleic anhydride in refluxing toluene gave the adduct, m.p. 117–118°.

TABLE VI

ATTEMPTED SYNTHESES OF *trans*-PHENYLBUTADIENE SULFONE

Expt.	Mole ratio: PB/SO_2	Temp., °C.	Time
1	1/3	Room	21 days
2	1/3	100	1.5 hr.
3	1/3	100	8 hr.
4	1/7	Room	17 days
5	1/106	100	15.5 hr.

Experiments 1–6, Table VII, on the polysulfone were carried out either by bubbling sulfur dioxide through an absolute ethanol solution of the hydrocarbon and catalyst or by sealing the reactants in a pressure bottle. The silver nitrate catalyst was about 1% with respect to the hydrocarbon; the ammonium nitrate, about 0.3%. In Expt. 6 3 ml. of peracetic acid solution, made from hydrogen peroxide, acetic anhydride and *p*-toluenesulfonic acid, 9.8 g. of phenylbutadiene, and 3 ml. of sulfur dioxide were allowed to react.[17] After evaporation of the solvent qualitative sulfur tests on the residues were negative. In Expt. 2 a precipitate formed, possibly a phenylbutadiene–silver nitrate addition compound.[18]

When 2,3-dimethylbutadiene was allowed to react under the conditions of Expt. 3, Table VI, 8.9 g. (56% of the theoretical yield) of cyclic sulfone, m.p. 134–135°,[19] were obtained. This hydrocarbon gave the polysulfone under the conditions of Expt. 1, Table VII, as a white amorphous alcohol-insoluble solid.

TABLE VII

ATTEMPTED SYNTHESES OF *trans*-PHENYLBUTADIENE POLYSULFONE

Expt.	Catalyst	Temp., °C.	Time	Method
1	$AgNO_3$	0	3 hr.	SO_2 bubbled in
2[a]	$AgNO_3$	Room	7 days	Press. bottle
3[a]	NH_4NO_3	Room	14 days	Press. bottle
4	NH_4NO_3	0	4 hr.	SO_2 bubbled in
5[a]	$AgNO_3$	Room	40 days	Press. bottle
6[a]	CH_3COOOH	Room	7 days	Press. bottle

[a] Mole ratio of reactants: 1/1.

The sulfur dioxide-catalyzed polymerization was run for Expt. 1, Table IV, by sealing 1 ml. of *trans*-phenylbutadiene and 1.5 ml. of liquid sulfur dioxide in a glass tube, opening and removing one drop samples for refractive index measurements. In Expt. 2 a fine stream of sulfur dioxide was bubbled through 20 ml. of phenylbutadiene, and a blank experiment with purified nitrogen gas was run in the same way. Air was excluded in both runs. For measuring the index sulfur dioxide was removed by bubbling nitrogen through a 0.5-ml. sample.

Since the solubility of sulfur dioxide in phenylbutadiene is significant, it was determined approximately by saturating samples at room temperatures, extracting with water, oxidizing sulfurous to sulfuric acid, and titrating.[20] Duplicate analyses showed 12.8 and 13.2% by weight of sulfur dioxide.

Photochemical Isomerization of *trans*-Phenylbutadiene.—To determine if ordinary laboratory daylight illumination affected the *trans* isomer a 95% ethanol solution containing 4 mg./l. was prepared in the dark, and this was compared in the spectrophotometer with a similar solution made under normal conditions. The absorption spectrum obtained from the first solution coincided exactly with the second (Fig. 1).

Exposure to summer sunshine of similar ethanol solutions in Pyrex flasks for 2 and 6 hours gave ultraviolet absorption spectra which approached that of the *cis* isomer (Fig. 1).

For indoor experiments a Hanovia ultraviolet lamp, type 16200, and a General Electric type H-4 mercury lamp were used. After several preliminary experiments the large-scale preparation of the *cis* isomer described below was carried out.

***cis*-1-Phenyl-1,3-butadiene.**—Two liters of 95% ethanol solution containing 163.3 g. of *trans*-phenylbutadiene was

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[17] Böeseken, Coden and Kip, *Rec. trav. chim.*, **55**, 815 (1936); Marvel and Clavis, THIS JOURNAL, **60**, 2622 (1938).

[18] Winstein and Lucas, *ibid.*, **60**, 836 (1938).

[19] Backer and Bottema, *Rec. trav. chim.*, **51**, 294 (1932).

[20] Taylor and Johnstone, *Ind. Eng. Chem., Anal. Ed.*, **1**, 197 (1929).

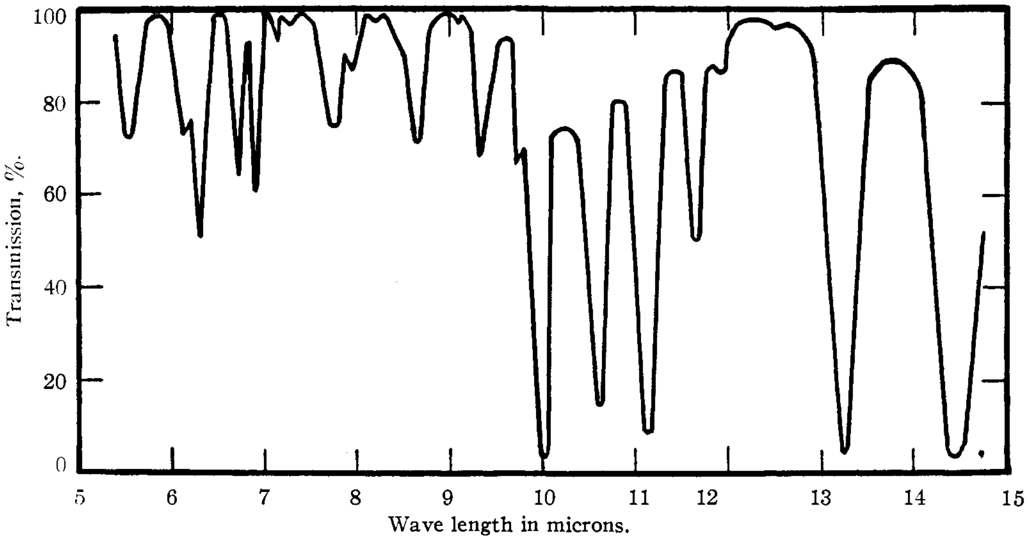

Fig. 4.—Infrared absorption spectrum of *trans*-phenylbutadiene.

stirred in a 3 l. three-necked Pyrex flask irradiated by two Hanovia lamps located at opposite sides of the flask and 4" from the flask walls. An electric fan directed at the flask held the temperature at about 36°. After six days an equal volume of water was added and the product recovered by extraction with Skellysolve A. Removal of the solvent gave 134.7 g. of mixed isomers and polymer. Distillation at 67–90° (2 mm.) gave 84.3 g., $n^{25}{}_D$ 1.5987. This was treated with two successive portions of maleic anhydride, 31.7 g. and 10.4 g., allowing one week at 0° for each reaction. The adduct was removed by filtration, the mixture was extracted with 5% sodium hydroxide until alkaline, and then washed with water. Five-tenths gram of solid methylmagnesium bromide was added before distillation from a Hickman pot still at 0.2 mm. The yield was 16.9 g., 10.3% of the quantity taken. Redistillation from a Claisen flask showed a distilling temperature of 42–43° (1 mm.); $n^{25}{}_D$ 1.5795.

Further purification was effected by adsorption with alumina. The distillate, dissolved in 75 ml. of Skellysolve B, was allowed to pass through a 1.5 × 50 cm. column of 80–200 mesh alumina (Grade F-20, Aluminum Co. of America). The recovered hydrocarbon showed $n^{25}{}_D$ 1.5817, $d^{25}{}_4$ 0.9200. A second treatment followed by distillation from the Hickman still gave a product of $n^{25}{}_D$ 1.5822, $d^{25}{}_4$ 0.9197. The absorption spectra and other physical properties are given in Figs. 1 and 3 and Table II.

Anal. Calcd. for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 91.95; H, 7.64.

Quartz offered no advantage over Pyrex in the irradiation. The yield of *cis* compound could probably be improved by vacuum stripping adsorbed hydrocarbon from the maleic anhydride *trans* adduct.

Iodine-Catalyzed Isomerizations of *trans*-1-Phenyl-1,3-butadiene.—A solution of 10 g. of *trans*-phenylbutadiene ($n^{25}{}_D$ 1.6087), 0.1 g. of iodine and 100 ml. of pure benzene was refluxed for seven hours under ordinary laboratory light. Removal of the solvent and vacuum distillation gave 8 g. of distillate at 58.5–59.0° (1.5 mm.), $n^{25}{}_D$ 1.6084. The ultraviolet absorption spectrum was identical with that for the *trans* isomer (Fig. 1). In a second experiment the reflux time was increased to 43 hours. The recovered phenylbutadiene showed no change in distilling temperature, refractive index or ultraviolet absorption.

***cis*-1-Phenyl-1,3-butadiene Plus Maleic Anhydride.**—A quantitative measure of the amount of maleic anhydride consumed in refluxing toluene after four hours, determined in the same way as for the *trans* isomer, gave 4.3 and 5.2% of of the theoretical quantity from duplicate experiments. At room temperature after one week no maleic anhydride was consumed.

***cis*-1-Phenyl-1,3-butadiene Plus Sulfur Dioxide.**—A mixture of 1.0 g. (7.7 millimoles) of the *cis* isomer, 7.0 g. (71 millimoles) of sulfur dioxide, 0.05 g. of phenyl-β-naphthylamine and 5.0 ml. of purified ether was allowed to stand in a pressure bottle at room temperature for one month. Working up the brown, tarry product gave no sulfone. A silver nitrate catalyzed experiment similar to Expt. 1, Table VII, gave no polysulfone.

Tetrabromide Derivatives.—Prepared by adding a 25% excess of bromine dropwise to the hydrocarbon dissolved in carbon tetrachloride and held at 0–10°. Three crystallizations from 95% ethanol of the product from the *trans* form gave colorless crystals melting 146.0–147.5°; the published melting point is 146°.[21] The tetrabromide from the *cis* after four crystallizations melted 147.2–147.7°. A mixed melting point showed no depression.

Determination of Physical Properties and Absorption Spectra.—Distilling temperatures were found on the purified isomers containing 0.1% of phenyl-β-naphthylamine by simple distillation from a 25-ml. cone-shaped Claisen flask with the pressure held constant by a manostat. Refractive index was measured with an Abbe refractometer held at 25 ± 0.1°.

Density was found with a calibrated Ostwald pycnometer at 25 ± 0.02°. Freezing points were determined from cooling curves measured by the National Bureau of Standards' method[22] which employs a platinum resistance thermometer and Mueller bridge. Fifty-five milliliters of the *trans* and 30 ml. of the *cis* isomer were used. The *trans* crystallized readily but the *cis* tended to supercool and required seeding.

Ultraviolet absorption spectra were measured on 95% ethanol solutions (4 mg. of hydrocarbon per liter) by a Beckman model DU quartz spectrophotometer. Infrared absorption spectra were found with a Beckman model IR-2 spectrophotometer in which the cell thickness was 0.03 mm. A rock salt blank was used.

Discussion

The estimated purity of the *cis*- and *trans*-phenylbutadienes, based on the reaction with maleic anhydride and the character of the cooling curves, is 99%.

The shift in maximum absorption to a shorter wave length and the decrease in specific extinction in the ultraviolet spectra, which accompany the *trans*→*cis* transformation, is similar to the geometric isomers of 1,4-diphenyl-1,3-butadiene.[23] While most of the bands in the infrared spectra occur at approximately the same wave lengths, each spectrum possesses unique bands. The 14.20 μ band for the *cis* isomer and the 10.56 μ band for

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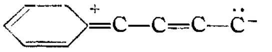
[21] Heide, *Ber.*, **37**, 2101 (1904).

[22] Glasgow, Krouskop, Beadle, Axilrod and Rossini, *Anal. Chem.*, **20**, 410 (1948).

[23] Pinckard, Wille and Zechmeister, THIS JOURNAL, **70**, 1938 (1948).

the *trans* may be due to the configurational difference.

The *cis* isomers of most olefins and of piperylene have higher values for the boiling point, refractive index, and density than the *trans* isomers. For the phenylbutadienes the opposite order has been found. Steric inhibition of resonance is a possible factor in determining the lower refractive index and molar refraction for *cis*-phenylbutadiene. Contributing forms in which there is a double bond between the ring and the *alpha* carbon atom, *e.g.*,



require a coplanar arrangement of the ring and side chain. In the *cis* configuration the phenyl and vinyl groups are too bulky, as shown by molecular models, to allow coplanarity, with the result that the contributions of such structures is reduced. It seems reasonable that this restriction on electron mobility (*i.e.*, reduced polarizability) would be reflected in a lower refractive index, molar refraction and boiling point.

Another consequence of this inhibition of resonance and reduced coplanarity is the decrease in wave length of maximum absorption and the degree of absorption in the ultraviolet region, as has already been demonstrated in the case of ortho-substituted benzoic acids,[24] benzils[25] and ortho and alpha substituted styrenes.[26]

Acknowledgment.—The authors wish to thank the du Pont Company for a fellowship, 1948–1949, E. C. Hughes and R. C. Foreman of the Standard Oil Company of Ohio for the infrared spectra, and L. C. Gibbons and J. F. Thompson of the N.A.C.A. Laboratory, Cleveland, for the freezing point determinations.

(24) Ross, THIS JOURNAL, **70**, 439 (1948).

(25) Leonard and Blout, *ibid.*, **72**, 484 (1950).

(26) Hirschberg, *ibid.*, **71**, 3241 (1949).

CLEVELAND, OHIO RECEIVED MAY 29, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Diamagnetic Anisotropy of Polyethylene, Polystyrene and Poly-2,5-dichlorostyrene

BY ELIZABETH M. WEIR[1] AND P. W. SELWOOD[2]

Measurements of diamagnetic anisotropy have been made on polyethylene, polystyrene and poly-2,5-dichlorostyrene. The samples used were in the form of fibers in several stages of elongation. Measurements were made by the Krishnan flip method. Calculations have been made of the anisotropy to be expected for several molecular orientations. Orientations of the aromatic groups in the two polystyrenes have been computed from the experimental data. Stretched polyethylene shows an almost negligible anisotropy, stretched polystyrene shows a small anisotropy and stretched poly-2,5-dichlorostyrene shows a large anisotropy. A few measurements of average (powder) susceptibilities have been made by the Faraday method.

A diamagnetic substance is one in which the magnetic flux density within the substance is less than in an impressed field surrounding it. The magnitude of the diamagnetism depends upon the average effective radius of the electronic orbits of the individual atoms. When the arrangement of the atoms in a substance is such that the average electronic radius is not the same in all directions in space, the substance has different magnetic susceptibilities along different directions and is therefore magnetically anisotropic. A completely amorphous high polymer will be magnetically isotropic, but as soon as it becomes oriented it will be anisotropic. An undrawn polymer fiber is nearly isotropic but, as the fiber is drawn, the orientation increases and the anisotropy becomes greater. The effect is especially noticeable in polymers containing aromatic groups because aromatic rings have a large magnetic anisotropy. Measurements of diamagnetic anisotropy are thus of use in determination of molecular orientation in certain classes of high polymers.

Experimental Part

Preparation of Samples.—Description, source and preparation of the several high polymer samples were: Polyethylene "unoriented monofilament"[3] was cut from the original coil into cylindrical rods about 8 mm. long and 1 mm. in diameter. The long axis of the samples was the long axis of the original material.

Polyethylene "monofilament machine stretched 249%"[3] was cut in rods, three or four of which were fastened together to form a bundle. The long axis of the sample was in the direction of stretching.

Polyethylene "partially drawn 280% elongation"[4] was cut from much longer rods. The long axis of the samples was in the direction of stretching.

Polyethylene "fully drawn 520% elongation"[4] was similarly cut from long rods. The long axis was in the direction of stretching.

Polyethylene "monofilament machine-stretched 574%"[3] was in the form of filaments which were wound several times around a frame, then tied and cut off in bundles 6 to 8 mm. long. Again the long axis was in the direction of stretching.

Polystyrene "unoriented monofilament"[4] was in the form of brittle cylindrical rods. Short sections about 5 mm. long were cut off with a razor blade. The long axis of the sample was the long axis of the original rod.

Polystyrene "monofilament machine-stretched 980%"[4] was made into fiber bundles large enough for measurement. The long axis of the bundles was in the direction of stretching.

Poly-2,5-dichlorostyrene "drawn about 500%"[4] was in the form of bars a few cm. long and with a cross-section of 2-3 mm.[2] Samples were cut 6 or 7 mm. long. The long axis was in the direction of stretching. It should be mentioned that the use of a razor blade to cut hard material often introduces a minute but extremely undesirable trace of strongly ferromagnetic steel. Careful washing of samples generally removes this difficulty.

Magnetic Anisotropy Measurements.—These were made by the Krishnan second, flip-angle, method.[5] Details of the

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[1] The award of the du Pont Company Postgraduate Fellowship in Chemistry is gratefully acknowledged.

[2] Inquiries concerning this paper should be addressed to P. W. Selwood.

[3] Supplied by the Bakelite Division, Union Carbide and Carbon Corporation, through the courtesy of Dr. V. E. Meharg.

[4] Supplied by the Bell Telephone Laboratories through the courtesy of Dr. W. O. Baker.

[5] K. S. Krishnan, B. C. Guha and S. Banerjee, *Phil. Trans. Roy. Soc. (London)*, **A231**, 235 (1933); **A234**, 265 (1935).