SHORT COMMUNICATIONS

Three Geometrical Isomers of p-Distyrylbenzene

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Three geometrical isomers are possible in *p*-distyrylbenzene (I) with regard to the ethylenic double bonds of the molecule. We have studied the synthesis and the photoisomerization of these three isomers with the purpose to compare the physical and chemical properties with those of the recently extensively studied pure polyolefinic systems such as diphenylpolyenes[1] and carotenoids[2].

The *cis, cis-* and *cis, trans*-isomers (I_c and I_b) were prepared by the partial hydrogenation of the corresponding acetylenic compounds using Lindlar's catalyst. The *trans, trans*-isomer (I_a) was obtained by the dehydration of *p*-bis(β-phenyl-α-hydroxyethyl)benzene. The isomers were purified by repeated recrystallization or chromatography on alumina.

Unexpectedly the sequence of qualitative photostability of these isomers under diffused light was found to be *trans, cis* (I_b) $\ll$ *cis, cis* (I_c) $\leq$ *trans, trans* (I_a). Both of the sterically hindered *cis, cis-* and *cis, trans*-isomers (I_c and I_b) showed no fine structure in their ultraviolet spectra as illustrated in Fig. 1. The *cis, trans*-isomer (I_b) showed the most intense *cis*-peak[2b] (ca. 270mμ) in accord with the theory proposed by Zechmeister.

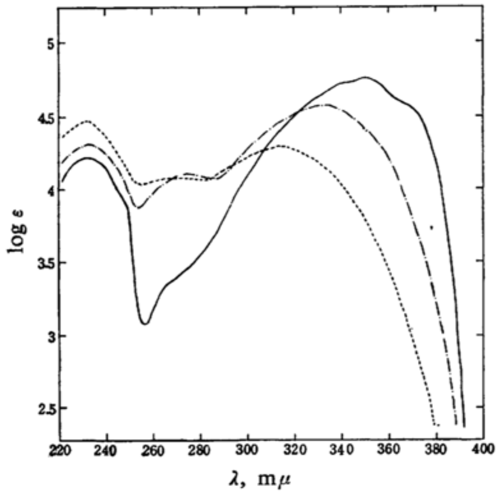

Fig. 1. Ultraviolet absorption spectra of *p*-distyrylbenzene (I) in *n*-hexane: ——, *trans, trans*; —·—, *cis, trans*; ----, *cis, cis*.

The solutions of the isomers were exposed to light of a fluorescent tube under controlled conditions and the course of the photoisomerization was followed by the change of the intensities of absorption at 270 and 350 mμ. The results are illustrated in Figs. 2 and 3. It is to be noted that the rate of spatial rearrangement of the most hindered *cis, cis*-isomer (I_c) is much slower than that of *cis, trans*-isomer (I_b). Theoretically, the same equilibrium mixture

TABLE I. PHYSICAL PROPERTIES OF *p*-DISTYRYLBENZENE

Isomer	*trans, trans*[3]	*trans, cis*[4]	*cis, cis*
m. p. (°C)	266~267	114~114.5	86.5~87.5
U. V. λ_{max}(mμ)	232, 350	232, 273, 331	232, 270, 314
(log ε)	(4.21), (4.76)	(4.09), (4.30), (4.56)	(4.44), (4.04), (4.22)
I. R. (cm⁻¹) *cis* δ_{CH}	—	774	774
trans δ_{CH}	966	961	—
Found* C,	93.59	93.58	93.79
H,	6.76	6.44	6.60

* Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43%.

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1) L. Zechmeister et al., *J. Am. Chem. Soc.*, **64**, 2755 (1942); **69**, 553 (1947); **70**, 1937 (1948); **76**, 2308, 4144 (1954); B. C. L. Weedon et al., *J. Chem. Soc.*, **1959**, 933.

2) a) L. Zechmeister, *Chem. Revs.*, **34**, 267 (1944); *Experientia*, **10**, 1 (1954).

b) L. Zechmeister, A. L. LeRosen, W. A. Schroeder, A. Polgar and L. Pauling, *J. Am. Chem. Soc.*, **65**, 1940 (1943).

3) H. Kaufmann, *Ber.*, **50**, 515 (1917); G. Drefahl and G. Plötner, *Chem. Ber.*, **91**, 1274 (1958); T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, **24**, 1246 (1959).

4) J. Dale, *Acta Chem. Scand.*, **11**, 971 (1957). He suggested that a compound melting at ca. 95°C, isolated from the products of photoisomerization of the *trans, trans*-isomer, may have the *cis, trans*-configuration.

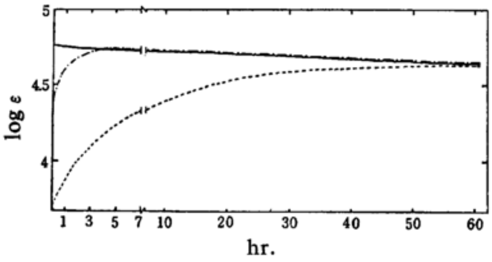

Fig. 2. Change of the extinction value at 350 mμ. of the U. V. spectra of three isomeric *p*-distyrylbenzenes in *n*-hexane by exposure to light: ——, *trans, trans*; —·—, *cis, trans*; ----, *cis, cis*.

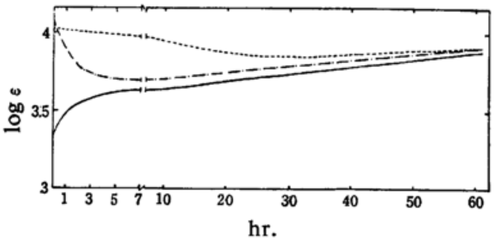

Fig. 3. Change of the extinction value at 270 mμ. of the U. V. spectra of three isomeric *p*-distyrylbenzenes in *n*-hexane by exposure to light: ——, *trans, trans*; —·—, *cis, trans*; ----, *cis, cis*.

might be attained regardless of the geometry of the starting isomers, but the experimental results showed a slight difference in their absorption spectra in final stage. This fact is attributable to the minor degree of decomposition or polymerization of I during the course of photostereomutation.

The experimental detail and the full discussion of this investigation will be published in near future.

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