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Stereoisomeric Diphenyloctatetraenes. Part II

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1,8-Diphenyloctatetraene undergoes *trans* → *cis* isomerization. Three chromatographically homogeneous, fluorescent *cis* forms (one of them crystalline) are described and discussed from the viewpoint of relative thermo- and photostabilities and the behavior in iodine-catalyzed solutions. They are assigned configurations that satisfy the spectral characteristics. In this and similar stereoisomeric sets "hindered" *cis* forms arise by direct rearrangement of the all-*trans* compound.

A first contribution to the stereochemistry of 1,8-diphenyloctatetraene,[1] $C_6H_5 \cdot \overset{(1)}{CH}{=}\overset{(2)}{CH}{-}\overset{(3)}{CH}{=}\overset{(4)}{CH}{-}\overset{(5)}{CH}{=}\overset{(6)}{CH}{-}\overset{(7)}{CH}{=}\overset{(8)}{CH} \cdot C_6H_5$, was made, in collaboration with the late Dr. A. L. LeRosen twelve years ago.[2] The experiments that had to be interrupted then, have now been carried through to what seems to be a reasonable completion. Three *cis* forms have been prepared for which configurations can now be proposed. The present study parallels our earlier investigations of stereoisomeric 1,4-diphenylbutadienes,[3] $C_6H_5 \cdot (CH{=}CH)_2 \cdot C_6H_5$, 1,6-diphenylhexatrienes[4] $C_6H_5 \cdot (CH{=}CH)_3 \cdot C_6H_5$, and some symmetrical azines.[5]

As pointed out earlier,[2] a *trans* → *cis* rearrangement of a "terminal" double bond (adjacent to a phenyl group) encounters steric hindrance, due to a spatial conflict between an aliphatically bound H-atom and an *ortho* ring hydrogen[2]; hence, the nine possible *cis*-diphenyloctatetraenes may be subdivided into seven "hindered" and two "unhindered" forms. It has been learned since the appearance of our Part I[2] that neither the steric hindrance just mentioned[6] nor that involving methyl groups[7] in isoprenic polyenes is an absolute one. Indeed, several such isoprenic "hindered" spatial forms have been obtained recently by total synthesis.[8] Sterically hindered *cis* compounds are characterized by a degraded spectrum, *i.e.*, very low extinction maxima, little or no fine structure in the main band, and an abnormally large wave length difference at λ_{max} from the all-*trans* spectrum; a *cis*-peak[9] may or may not be present depending on the over-all shape of the molecule.

Ordinary (all-*trans*) diphenyloctatetraene yields three fluorescent, chromatographically separable *cis* forms termed, in the sequence of decreasing adsorption affinities I-III, when submitted to the treatments listed in Table I. *cis*-I formed large crystals (m.p. almost 100° lower than that of the all-*trans* compound); *cis*-II is a powder, probably microcrystalline, while *cis*-III is oily.

all-*trans*-Diphenyloctatetraene, like all-*trans*-diphenylhexatriene, is more thermostable in solution than any of its *cis* isomers, although it is somewhat light-sensitive (Table I). The stability of *cis*-I is comparable to that of the all-*trans* compound but *cis*-II and -III are markedly more thermo- and photolabile. Concentrated *cis*-II solutions can be kept at 4°, in darkness, for several days without marked rearrangement while *cis*-III undergoes considerable spatial change under these conditions.

cis-I-Diphenyloctatetraene melts at 139–141° (cor.); however, it resolidifies soon and upon further heating remelts near the m.p. of the all-*trans* compound (235–237°) which was formed by *cis* → *trans* rearrangement during the melt. *cis*-II melts gradually between 70 and 80°, and shows a second m.p. near 190°.

Each of the three *cis* forms displays sharply differentiated spectral features[10] (Table II). The *cis*-I curve shows (Fig. 2) marked fine structure which indicates that no terminal (hindered) *cis* double bond can be present. Hence, this isomer could *a priori* represent either the central mono-*cis* (*β*, Fig. 1) or the central di-*cis* (3,5-di-*cis*) form. We propose for *cis*-I the 3-mono-*cis* configuration *β*, considering the very small difference (1–2 mμ) between the positions of λ_{max} of this form and the all-*trans*-diphenyloctatetraene, and mainly because of the very high *cis*-peak, the highest observed in this set, that would be in contradiction to the straight over-all molecular form of the di-*cis* compound mentioned.

The extinction curve of the *cis*-II isomer (Fig. 3) represents a typical degraded spectrum with very low extinction values and practically no fine structure in the main band. Such degraded spectra may or may not include a *cis*-peak, depending on the straight or bent molecular form.[4,5] In the *cis*-II curve under discussion a moderate *cis*-peak is present. It excludes the configurations D and E in Fig. 1 (1,3- and 1,5-di-*cis*) that correspond to a straight molecular type. We assign to the *cis*-II isomer the 1-mono-*cis* configuration (C in Fig. 1).[11]

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(1) For the synthesis of the all-*trans* form of this compound, *cf.*, R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 87 (1928).

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

(3) A. Sandoval and L. Zechmeister, *ibid.*, **69**, 553 (1947); J. H. Pinckard, B. Wille and L. Zechmeister, *ibid.*, **70**, 1937 (1948).

(4) K. Lunde and L. Zechmeister, *ibid.*, **76**, 2308 (1954).

(5) J. Dale and L. Zechmeister, *ibid.*, **75**, 2379 (1953).

(6) Although the existence of *cis*-1,4-diphenylbutadienes has been established a long time ago by F. Straus, *Ann.*, **342**, 190 (1905), this compound represents a special type since its "hindered" double bonds are without competition from "unhindered" bonds.

(7) L. Pauling, *Fortschr. Chem. organ. Naturstoffe*, **3**, 203 (1939).

(8) *Cf. e.g.*, W. Oroshnik, G. Karmas and A. D. Mebane, THIS JOURNAL, **74**, 295, 3807 (1952); **75**, 1050 (1953); C. H. Eugster, C. F. Garbers and P. Karrer, *Helv. Chim. Acta*, **35**, 1179 (1952); C. F. Garbers, C. H. Eugster and P. Karrer, *ibid.*, **35**, 1850 (1952); **36**, 562 (1953); C. F. Garbers and P. Karrer, *ibid.*, **36**, 828 (1953).

(9) L. Zechmeister and A. Polgár, THIS JOURNAL, **65**, 1522 (1943); L. Zechmeister, A. L. LeRosen, W. A. Schroeder, A. Polgár and L. Pauling, *ibid.*, **65**, 1940 (1943).

(10) Infrared spectra of the isomers described will be published in collaboration with K. Lunde.

(11) In our Part I, a 3,5-di-*cis* configuration was tentatively considered for this compound[2] (then termed "Zone 3"). However, at that time it had to be assumed that the steric hindrance of terminal double bonds was an absolute one.

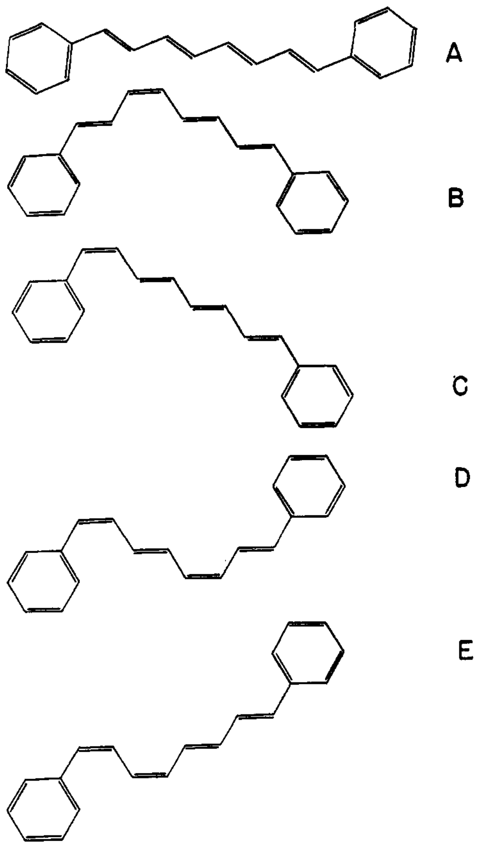

Fig. 1.—Skeleton models of some 1,8-diphenyloctatetraenes: A, all-*trans;* B, 3-mono-*cis* (configuration assigned to *cis*-I); C, 1-mono-*cis* (assigned to cis-II); D, 1,5-di-*cis* and E, 1,3-di-*cis* (possible configurations for *cis*-III); assigned, 1,3- or 1,5-di-*cis*.

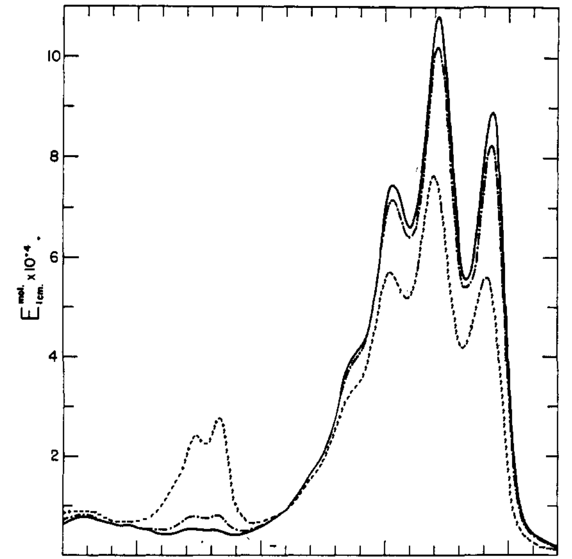

Fig. 2.—Molecular extinction curves of all-*trans*- and *cis*-I-diphenyloctatetraene in hexane: ———, fresh solution of all-*trans;* - - - - -, fresh solution of *cis*-I; and - · - · -, mixture of stereoisomers after 15 min. iodine catalysis of either form.

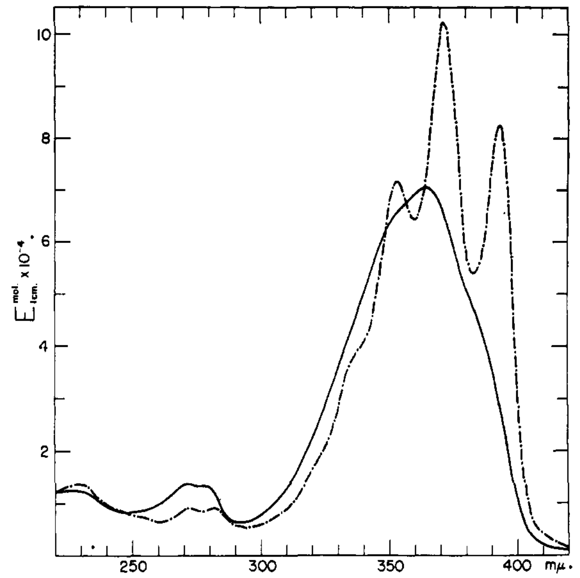

Fig. 3.—Molecular extinction curves of *cis*-II-diphenyloctatetraene in hexane: ———, fresh solution; and - · - · -, mixture of stereoisomers after 15 min. iodine catalysis.

It is remarkable that the wave length difference between the all-*trans* and a hindered *cis* form at λ_{max} is much smaller in the stereoisomeric set under discussion than in those of stilbene,[12] diphenylbutadiene and diphenylhexatriene (~ 15 mμ, in hexane).

Finally, on the basis of Fig. 4 (no fine structure, no *cis*-peak, difference from the main bands of all-*trans* and this isomer, 12 mμ) a hindered-unhin-

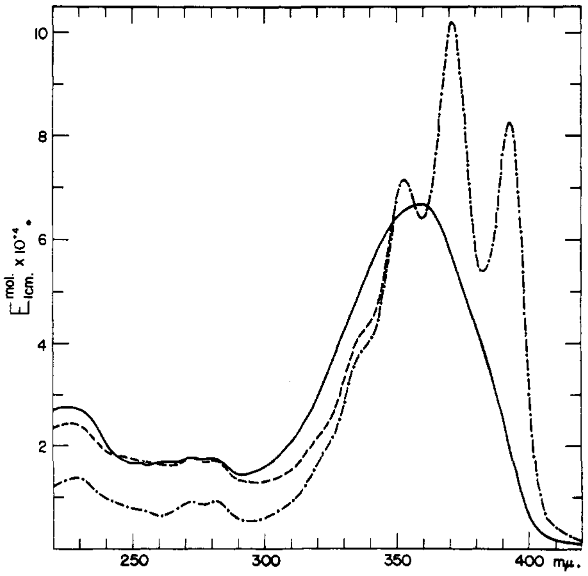

Fig. 4.—Molecular extinction curves of *cis*-III-diphenyloctatetraene in hexane: ———, fresh solution; - - - - -, mixture of stereoisomers after 15 min. iodine catalysis of *cis*-III; and - · - · -, mixture of stereoisomers after catalysis of all-*trans*. (Minor impurities seem to be responsible for the higher extinction values of the two *cis*-III curves in the far ultraviolet.)

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[12] A. Smakula and A. Wassermann, *Z. physik. Chem.*, **A155**, 353 (1931).

dered di-*cis* configuration is proposed for *cis*-III-diphenyloctatetraene; however, we are unable to give preference either to the 1,3- or to the 1,5-di-*cis* form (D and E in Fig. 1).

It has been pointed out by Lunde and one of the writers[4] that configuration assignments based on spectra in the diphenylhexatriene set may be tested and confirmed by a study of the relative rates of the iodine-catalyzed rearrangement to give the equilibrium mixture. It was found that these rates were sharply dependent on the configuration and especially on the nature of *cis* double bond(s) present, in the sense that a hindered *cis* double bond rearranged much more rapidly than an unhindered one.

Such a statement is also valid in the diphenyloctatetraene set as demonstrated in Figs. 5 and 6. Figure 5 refers to extinction values obtained in the main band region and Fig. 6 to the *cis*-peak region. Evidently, all curves listed approach gradually that corresponding to the equilibrium mixture containing 86% all-*trans* and 14% *cis* forms.

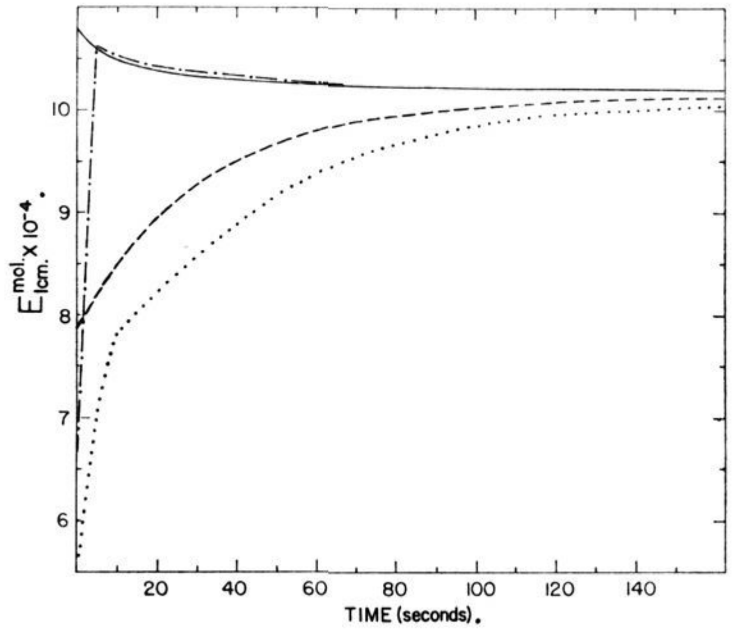

Fig. 5.—Change of molecular extinction values at 371 mμ (in hexane) during iodine catalysis of some stereoisomeric diphenyloctatetraenes: ———, all-*trans*; - - - - -, *cis*-I; - · - · -, *cis*-II; and . . . . . *cis*-III.

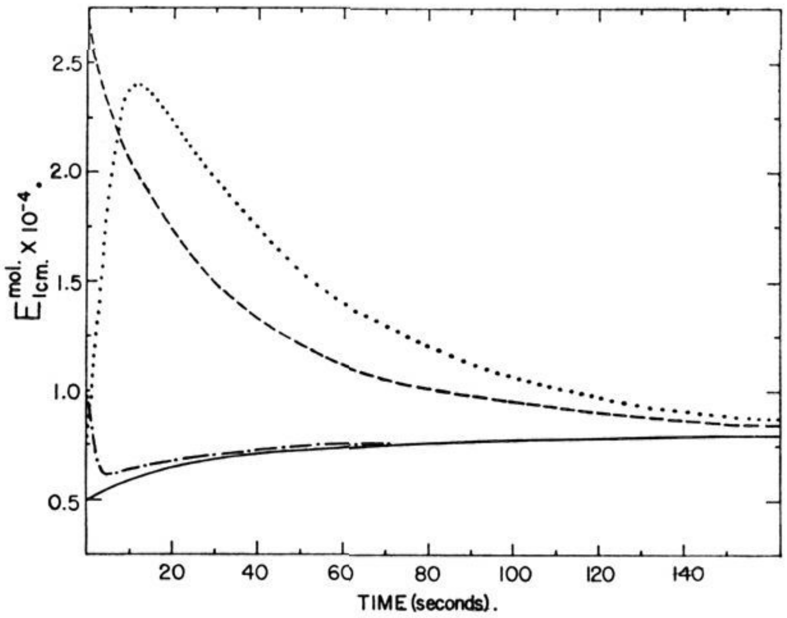

Fig. 6.—Progressing changes in the height of the *cis*-peak upon iodine catalysis (measured at 283 mμ, in hexane): ———, starting from all-*trans*-diphenyloctatetraene; - - - - -, from *cis*-I; - · - · -, from *cis*-II; and . . . . . ., from *cis*-III.

TABLE I

THE RELATIVE COMPOSITION OF STEREOISOMERIC MIXTURES OF DIPHENYLOCTATETRAENES OBTAINED FROM THE ALL-*trans* FORM

Treatment (for conditions, *cf.* the Experimental Part)		Resulting amounts of the steroisomers (recovered material = 100%)				Recovery % (starting material = 100%)
		Unchanged all-*trans*	*cis*-I	*cis*-II	*cis*-III	
Iodine catalysis	(15 min.)	86.2	11.1	2.2	0.5	99
Iodine catalysis	(30 min.)	86.0	11.5	2.0	.5	93
Iodine catalysis	(1 hr.)	87.3	10.1	2.2	.4	89
Insolation	(1 hr.)	88.8	8.6	2.2	.4	76
Insolation	(2.5 hr.)	88.7	9.2	1.7	.4	60
Irradiation	(15 min.)	92.5	6.2	1.1	.2	98
Irradiation	(1 hr.)	88.5	9.7	1.5	.3	96
Irradiation	(4 hr.)	87.9	9.9	1.9	.3	91
Melting crystals	(5 min.)	77.3	22.0	0.7	..	20
Melting crystals	(15 min.)	77.2	21.7	1.1	..	4
Refluxing in hexane	(30 min.)	96.8	3.2	..	..	98
Refluxing in benzene	(30 min.)	90.8	8.0	1.0	.2	96
Refluxing in xylene	(30 min.)	89.1	9.6	1.0	.3	93

The extinction values of the all-*trans* form decrease slowly in the main band and increase slowly in the *cis*-peak region while the all-*trans* compound is converted partially to *cis* forms. The extinction of *cis*-I rises slowly in the main band and decreases at the same rate in the *cis*-peak region as it rearranges mainly to all-*trans*. In contrast, the extinction of *cis*-II rises rapidly in the main band and then decreases slowly (Fig. 5), whereas in the *cis*-peak region it decreases rapidly at first and then increases slowly (Fig. 6). This indicates a fast and almost complete conversion of the *cis*-II form to all-*trans;* from this point on the curve almost coincides with that obtained by direct catalytic conversion of the *trans* form. Finally, the main band extinction of *cis*-III increases in two distinct steps, the first being fast and the second slow (Fig. 5). In the *cis*-peak area the extinction first increases very quickly; then the rate curve shows a sharp maximum (Fig. 6) and de-

Fig. 7.—Crystals of all-*trans*-diphenyloctatetraene (plates), and of the *cis*-I form (prisms). From chloroform–methanol; 430 ×.

TABLE II

SPECTRAL CHARACTERISTICS OF SOME STEREOISOMERIC DIPHENYLOCTATETRAENES (IN HEXANE)

		Main band			
Name	Configuration	Fine structure	Wave length position of λ_{max}, mμ	Wave length difference from all-*trans* at λ_{max}, mμ	Position of *cis*-peak, mμ
All-*trans*	All-*trans*	Very pronounced	371–372	. .	Very slight at 282–283 and 272 (Fig. 2)
cis-I	3-*cis*	Pronounced	369–370	2	283 and 273–274 (Fig. 2)
cis-II	1-*cis*	Slight indication	364	7–8	271–272 (Fig. 3)
cis-III	1,3- or 1,5-di-*cis*	None	359–360	12	Very slight maxima at 282 and 272–273 (Fig. 4)

creases slowly. This behavior is explained by a rapid conversion of *cis*-III to *cis*-I which intermediate then approaches the equilibrium mixture. All these observations are in agreement with the configuration assignments proposed.

In summary we wish to stress that in all *cis-trans* isomeric polyene sets studied so far, only certain of the theoretically possible configurations are preferred and appear upon rearrangement of the all-*trans* compound. Furthermore, the definition of hindered-unhindered *cis* isomers is not coincident with that of preferred-non-preferred isomers. This is illustrated, for example, by the presence of marked amounts of hindered *cis* forms in stereoisomeric diphenyloctatetraene or diphenylhexatriene (quasi-)equilibria, in addition to unhindered forms.

Experimental

Material and Methods.—The following adsorbents were used: a 1:1:1 mixture of magnesia (Seasorb 43; Food Mach. and Chem. Corp.), lime (Arrowhead, U. S. Lime Prod. Co., Los Angeles, Calif.) and Celite No. 545 (Johns-Manville); furthermore, a 2:1 lime–Celite mixture; a 2:1 magnesia–Celite mixture; and a 3:1 alumina–Celite mixture (Aluminum oxide, ignited, Merck's Reagent). For some experimental details, *cf.* also ref. 4. All operations should be carried out in darkness or dim light, and evaporations *in vacuo*, in darkness.

all-*trans*-Diphenyloctatetraene.[1]—Our starting material melted at 235° (cor., evacuated capillary; some dec.); $E^{\text{mol.}}_{1\text{ cm.}}$ 10.8 × 10^4 at λ_{max} (371–372 mμ, in hexane; *cf.* Fig. 2).

***cis*-I-Diphenyloctatetraene.** (a).—A solution of 350 mg. of the all-*trans* compound in 500 ml. of warm benzene was diluted with hexane to 2.5 l., exposed in ten 250-ml. Pyrex volumetric flasks to intense sunshine for 2 hr., and developed on a 30 × 7.2 cm. magnesia–lime–Celite column with benzene–hexane (2:1) and later with pure benzene, whereby the *cis*-II and III isomers washed into the filtrate. The *cis*-I compound formed a greenish 18-mm. zone, somewhat duller in fluorescence than the well-separated, unchanged 50-mm. all-*trans* top zone. The *cis*-I zone was, after cutting, eluted on a sintered glass funnel by washing alternately with alcohol and hexane until the flow had ceased to fluoresce. By adding water to the filtrate the substance was transferred quantitatively into hexane that was washed, dried and evaporated. The powdery, crystalline residue was dissolved in the minimum amount of chloroform at 25° and transferred into a centrifuge tube. Methanol was then added dropwise, with stirring, until the liquid became turbid, whereupon the addition was continued with cooling in ice-water. Long prisms began to appear. The suspension was diluted with methanol to 5–6 vol. per vol. chloroform and kept at 0° for a few hours. After centrifuging the sample was recrystallized as described; pale yellow prisms (Fig. 7), yield 17 mg., m.p. 139–141°.

Anal. Calcd. for $C_{20}H_{18}$: C, 92.97; H, 7.03. Found: C, 92.73; H, 6.97. $E^{\text{mol.}}_{1\text{ cm.}}$ 7.65 × 10^4 at λ_{max} (369–370 mμ, in hexane).

(b).—The all-*trans* compound (1.1 g. in 350 ml. of xylene) was refluxed for 2 hr.; then 7 vol. of hexane was added and the solution was kept in an ice-bath for 1 hr. Deposited crystals of the unchanged all-*trans* form were filtered off and the filtrate was developed on magnesia–lime–Celite (30 × 7.2 cm.) with 1.5 l. of benzene–hexane 2:1 (the figures on left designate thickness of zones, in mm.; fl. = fluorescent):

5 brown
3 empty
2 blue fl.
35 greenish fl.; unchanged all-*trans*
6 greenish fl.; *cis*-I
18 pale blue fl.
2 greenish fl.
12 empty
21 greenish fl.; *cis*-II
4 empty
9 pale green fl.; *cis*-III
7 empty
54 a blue fl. and a pale green fl. zone, well separated
100 empty
Filtrate: bluish fl.

The *trans* and *cis*-I zones were cut out together, eluted with benzene-ethanol, washed, dried and diluted with 3 vol. of hexane. This solution (1.8 l.) was adsorbed on magnesia–lime–Celite (30 × 7.2 cm.), developed with benzene–hexane 2:1 and later with pure benzene. The lower, *cis*-I zone was eluted, washed, dried, evaporated completely at 20°, and the powdery residue (*cis*-I) was crystallized from chloroform–methanol; yield 43 mg.

The *cis*-II and -III zones were cut out separately and eluted with benzene-ethanol. Each of these two eluates was washed, dried, combined with corresponding eluates obtained from two more 30 × 7.2 cm. columns (from parallel experiments) and transferred into benzene; *cf.* the next Sections.

The *cis*-I-diphenyloctatetraene crystals were stable at room temperature when exposed to air in scattered light for two weeks. In solutions only 3% of the substance rearranged to the all-*trans* form at 25° in 24 hr. Insolation of solutions containing 3 mg. per l. yielded the all-*trans* compound almost quantitatively within 45 sec. For isomerization in the melted states, *cf.* above.

***cis*-II-Diphenyloctatetraene.**—The combined benzene solutions of *cis*-II (see above) were evaporated completely. The residue (photosensitive!) was taken up in 0.5–1 ml. of chloroform, transferred to a 15-ml. centrifuge tube and cooled in ice-water, with stirring, while absolute methanol was dropped in. A powdery, probably micro-crystalline substance precipitated. After the addition of 5 vol. of methanol the solution was kept at 0° for an hour and centrifuged. The residue was recrystallized as described; yield 12 mg. Although this preparation was chromatographically homogeneous, it did not give correct analytical values (found: C, 91.86; H, 8.39). The sample softened over the range, 55–75°, resolidified at higher temperatures and melted again, with some darkening, at about 210°, *i.e.*, somewhat below the all-*trans* m.p. The molecular extinction values (Fig. 3) were determined indirectly, after iodine catalysis, by using the average values obtained for the corresponding equilibria starting from the all-*trans* and *cis*-I forms.

Solid *cis*-II preparations converted to the all-*trans* compound when kept at 25°, in darkness, for a few days. However, hexane solutions were much more stable; only 2–3% of the solute rearranged within several days when standing at 4°, in darkness. The stereoisomerization was markedly more rapid at 25°. Exposure to sunshine of a solution containing 3 mg. per l. yielded (mainly) the all-*trans* compound in 45 sec.

***cis*-III-Diphenyloctatetraene.**—The combined *cis*-III solutions (in benzene, see above) were evaporated to dryness, the oily residue was dissolved in a few ml. of hexane and developed with the same solvent on alumina–Celite (27 × 5.5 cm.). The *cis*-III zone was cut and eluted with benzene; the eluate was evaporated completely and the oily residue dissolved in optical grade hexane. *cis*-III-Diphenyloctatetraene could not be separated from traces of an impurity which absorbed light in the 220–300 $m\mu$ region (Fig. 4) but did not affect the main band. The molecular extinction values were determined as described for *cis*-II. In the absence of solvent the oily *cis*-III is very photosensitive and isomerizes spontaneously even at room temperature, in darkness. Much slower is the rearrangement in dilute hexane solutions (3 mg. per l.); under these conditions it amounted to 8% in a day. Insolation of dilute solutions yielded the all-*trans* form in 45 sec. The iodine catalysis induced a rearrangement in two distinct steps as shown in Figs. 5 and 6.

Methods of Isomerization and Estimation. (a) Insolation.—In order to determine the ratio of the stereoisomers formed a benzene solution of the all-*trans* compound (10 mg. per 25 ml.) was exposed in a Pyrex volumetric flask to bright sunshine (Table I), diluted with 4 vol. of hexane and developed on a 20 × 3.5 cm. magnesia–lime–Celite column with benzene–hexane 1:2. The following chromatogram is the result of insolation for 1 hr.

3 brownish yellow
1 blue fl.
15 green fl.; unchanged all-*trans*
4 somewhat weaker green fl.; *cis*-I
10 empty interzone
2 blue fl.
40 empty interzone
8 pale green fl.; *cis*-II
5 empty interzone
4 pale green fl.; *cis*-III
100 empty section

The *trans* and *cis*-I zones were cut out together, eluted, transferred to benzene-hexane 1:3 and developed on a 30 × 3.5 cm. column with pure benzene until the *cis*-I zone has separated from the upper (*trans*) zone. The *cis*-II and III zones were cut out separately, eluted and transferred to hexane. Each steric form was estimated photometrically after evaporating and re-dissolving in optical grade hexane.

(b) Iodine Catalysis.—A solution containing 1 mg. of all-*trans* form and 0.02 mg. of iodine in 100 ml. of hexane was exposed in a Pyrex flask to a fluorescent daylight lamp[4] from 60 cm. distance and developed with benzene–hexane 1:2 on an 18 × 2 cm. magnesia–lime–Celite column.

5 empty section
5 green fl.; unchanged all-*trans*
2 somewhat weaker green fl.; *cis*-I
30 empty interzone
6 pale green fl.; *cis*-II
10 empty interzone
7 pale green fl.; *cis*-III
110 empty section

The all-*trans* and *cis*-I forms had to be rechromatographed in order to obtain clear separation.

(c) Refluxing.—A hexane solution of 1 mg. of the all-*trans* form was refluxed in 100 ml. of hexane while nitrogen bubbled through. The solution was then chromatographed as just described. Solutions in benzene or xylene (1 mg. per 25 ml.) were diluted with 4 vol. of hexane before chromatography.

(d) Irradiation.—One mg. of the *trans* compound in 100 ml. of hexane, contained in a Pyrex volumetric flask, was illuminated by a Photoflood bulb No. 1 from 10 cm. distance while the flask was cooled with a stream of water, and then chromatographed.

(e) Melting Crystals.—A 10-mg. sample of the all-*trans* form, sealed in an evacuated tube, was immersed completely in an oil-bath at 255–260°, the contents were dissolved in benzene and, after the addition of 4 vol. of hexane, the solution was developed with benzene 1:2 on a 20 × 3.5 cm. magnesia–lime–Celite column. The combined all-*trans* and *cis*-I zones had to be rechromatographed before photometric estimation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Preparation of Some Imidazole Derivatives of 1,4-Naphthoquinone

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A series of 2-substituted-1H-naphthimidazole-4,9-diones has been synthesized as compounds having potential biological activity and their chemistry has been discussed.

The work presented here represents a continuation of our efforts to synthesize compounds which would compete with essential metabolites. The present paper reports the synthesis of a number of 1H-naphthimidazole-4,9-diones. It was thought that such compounds might interfere with the normal utilization of vitamin K or of the purines since they contain groups common to these two classes of compounds.

A number of 1,4-naphthoquinones have been shown to be metabolite antagonists and their activity is neutralized by the addition of vitamin K or 3-methyl-1,4-naphthoquinone. 2,3-Dichloro-1,4-naphthoquinone is a powerful fungicide.[1] 2-Methoxy- and 2-chloro-1,4-naphthoquinone display some antibiotic activity toward certain organisms.[2] Certain 2-alkyl-3-hydroxy-1,4-naphthoquinones have considerable antimalarial activity.[3] Benzimidazole and 5(6)-aminobenzimidazole were found to exhibit a bacteriostatic action which could be reversed by the addition of guanine or adenine.[4]

In view of the above reports, as tudy of the preparation of a number of 1H-naphthimidazole-4,9-diones appeared desirable. Little work appears in the literature on the preparation of the linear imidazoles of 1,4-naphthoquinone. The preparation of 1H-naphthimidazole-4,9-dione and 2-methyl-1H-naphthimidazole-4,9-dione was effected earlier, by the chromic acid oxidation of naphth(2,3)imidazole and 2-methylnaphth(2,3)imidazole.[5] The last two compounds were obtained by heating 2,3-diaminonaphthalene with formic acid and acetic acid, respectively. This did not appear to be a good method for the present investigation for two reasons: (1) the diamine is not easily obtainable, and (2) the introduction of oxidizable groups into the molecule would not be feasible because of the oxidative step.

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(1) D. W. Woolley, *Proc. Soc. Exptl. Biol. Med.*, **60**, 225 (1945).

(2) J. Guerillot-Vinet and Mme. J. Guerillot-Vinet, *Compt. rend.*, **227**, 03 (1948).

(3) L. F. Fieser, *et al.*, *Record Chem. Progress*, **7**, No. 314, 26 (1946); THIS JOURNAL, **70**, 3151 (1948).

(4) D. W. Woolley, *J. Biol. Chem.*, **152**, 225 (1944).

(5) K. Fries, R. Walter and K. Schilling, *Ann.*, **516**, 248 (1935).