covered. When isobutyromesitylene, b.p. 142–143° at 19 mm. (prepared in 75% yield by the Friedel–Crafts acylation of mesitylene with isobutyryl chloride),[11] was refluxed even for 20 hours with the acid mixture, 82% of the original ketone was recovered. A 2-g. residue was obtained, but no mesitylene was found.

DURHAM, NORTH CAROLINA

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[11] A. Klages, *Ber.*, **37**, 928 (1904).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1856]

cis-trans Isomeric 1,6-Diphenylhexatrienes

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RECEIVED NOVEMBER 16, 1953

1,6-Diphenylhexatriene[1,3,5] may assume six spatial configurations of which five were observed upon partial stereoisomerization of the ordinary (all-*trans*) form (m.p. 203°) and subsequent chromatographic resolution of the fluorescent stereoisomeric mixture. One of the new isomers, termed *cis*-I, has crystallized, two others (*cis*-II and -III) were isolated as oils in the pure state, while the existence of the minor isomer *cis*-IV could be ascertained by qualitative observations only. Some ultraviolet spectral characteristics including the fine structure and *cis*-peak effect of the individual spatial forms are given; the relative stabilities of the stereoisomers are discussed, including the behavior in iodine-catalyzed solutions; it is shown that when both hindered and unhindered *cis* double bonds are present, the former type is rearranged first. Configurations for three *cis* forms are proposed.

Although the three steric forms of diphenylbutadiene have been studied extensively[2] and some pertinent data are also available for diphenyloctatetraene,[3] so far as we know the stereoisomerization of 1,6-diphenylhexatriene-1,3,5, $C_6H_5{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}C_6H_5$, has not yet been investigated.

That the preparations obtained by synthesis represent the all-*trans* form, was demonstrated by X-ray analysis.[4]

As pointed out earlier, the *cis* forms of a diphenylpolyene may be subdivided into sterically "unhindered" and "hindered" types. When a terminal double bond of the open chain undergoes *trans* → *cis* rearrangement, a spatial conflict arises between a H-atom of the side chain and a ring hydrogen located in *o*-position to the aliphatic section.[5] Diphenylhexatriene offers the feature, unique in this series, that all but one of its possible *cis* configurations (2 mono-*cis*, 2 di-*cis* and 1 tri-*cis*) are "hindered," the sole exception being the central mono-*cis* isomer (*cf.* Fig. 5).

We find that ordinary (all-*trans*-) diphenylhexatriene can be partially converted into a mixture of stereoisomers by exposing its solutions to sunshine ("insolation"), by iodine catalysis in light, by melting crystals, or by the formation and subsequent cleavage of its boron trifluoride complex.[6] Refluxing in darkness does not produce sizable amounts of *cis* forms (Table I).

TABLE I

COMPOSITION OF SOME STEREOISOMERIC MIXTURES OBTAINED FROM ALL-*trans*-DIPHENYLHEXATRIENE BY *trans* → *cis* REARRANGEMENT

Treatment	Unchanged all-*trans*	Content in the mixture, % *cis*-I	*cis*-II	*cis*-III + *cis*-IV	Destruction products (by diff.)
Iodine catalysis[a]	93.5	1.7	3.7	0.3	1
Iodine catalysis[a]	93.9	1.8	3.8	.3	0.5
Insolation (60 min.)[b]	65.0	3.5	6.3	.5	25
Insolation (60 min.)[b]	62.0	3.3	6.6	.5	28
Refluxing (45 min.)[c]	Only traces of *cis* forms were obsd.				
Melting crystals[d]	10.5	0.5	2.3	0.1	87
Via the BF_3 complex[e] (10 min.)	24	.48	0.27	.48	75
Via the BF_3 complex[e] (60 min.)	2	.48	.34	.46	96

[a] For conditions *cf.* the Experimental part. [b] In hexane, 3 mg. per 100 ml. [c] In *n*-propyl alcohol, b.p. 97°, 7 mg. per 100 ml.; in darkness. [d] In a boiling diphenyl ether bath, b.p. 259°; duration, 15 min. (evacuated capillary tube). [e] The time given refers to the duration of the interaction of the substance and boron trifluoride etherate terminated by the addition of 95% methanol; *cf.* the Experimental part.

Of the five possible *cis* isomers, four have been observed in the present study; they are located below the all-*trans* zone on the chromatographic column and termed, in the order of decreasing adsorption affinities, *cis*-I to *cis*-IV. The differences between the adsorbabilities as well as the fluorescence behavior in ultraviolet light, made possible a chromatographic resolution of stereoisomeric mixtures. *cis*-I has been crystallized (m.p. 107°); the *cis* forms II and III were isolated as chromatographically homogeneous and spectroscopically pure oils, while the existence of the minor isomer *cis*-IV was secured by qualitative observations only.

All-*trans*-diphenylhexatriene is the most thermostable among the stereoisomers but it is light-sensitive to a limited extent. Under the conditions of refluxing in darkness, the *cis*-I configuration is definitely less resistant than those of the all-*trans* and *cis*-II compounds. In scattered light the stability of *cis*-I is comparable to that of the all-*trans*

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[1] Smith-Mundt Research Fellow (from the University of Oslo).

[2] F. Straus, *Ann.*, **342**, 190 (1905); C. Kelber and A. Schwarz, *Ber.*, **45**, 1946 (1912); E. Ott and R. Schröter, *ibid.*, **60**, 624 (1927); A. Sandoval and L. Zechmeister, THIS JOURNAL, **69**, 553 (1947); J. H. Pinckard, B. Wille and L. Zechmeister, *ibid.*, **70**, 1937 (1948).

[3] L. Zechmeister and A. L. LeRosen, *ibid.*, **64**, 2755 (1942).

[4] J. Hengstenberg and R. Kuhn, *Z. Kryst. Min.*, **75**, 301 (1930); **76**, 174 (1930).

[5] See Fig. 2 given in reference 3. For the existence of hindered *cis* forms of isoprenic polyene structures, *cf.* C. H. Eugster, C. F. Garbers and P. Karrer, *Helv. Chim. Acta*, **35**, 1179 (1952); **35**, 1850 (1952); **36**, 562 (1953). General discussion, L. Zechmeister, *Experientia*, **10**, 1 (1954).

[6] The interaction of diphenylpolyenes and BF_3 is under investigation. As Table I shows, in spite of progressive irreversible destruction the amount of the *cis* forms obtained after 10 min. and 60 min. is remarkably constant. For conversions of carotenoid pigments *via* their BF_3-complexes, *cf.* L. Wallcave, J. Leemann and L. Zechmeister, *Proc. Nat. Acad. Sci.*, **39**, 604 (1953); L. Wallcave and L. Zechmeister, THIS JOURNAL, **75**, 4495 (1953).

form; *cis*-II is much more light-sensitive. In the absence of solvents a few minutes exposure of oily *cis*-II samples to intense sunshine resulted in partial crystallization; the crystals were, however, those of the all-*trans* compound as identified by mixed chromatography. *cis*-III-Diphenylhexatriene shares the relatively high degree of photolability with *cis*-I and that of thermolability with *cis*-I.

When during the development process a *cis*-II or a *cis*-III zone was exposed, from a short distance, to ultraviolet light for a minute or so, the partial formation of a second all-*trans* zone was observed on the cylindrical surface of the column.

The ultraviolet spectra of these stereoisomers are characterized in Table II and Figs. 1–4. As stated earlier[7] the *cis*-peak is a measure of the bending of the polyene molecule. It is a remarkable feature, very rarely encountered in the field of the carotenoids, that there is a marked difference (5 to 7 mμ) in the locations of the respective *cis*-I and *cis*-II *cis*-peaks. The spectral curves of the all-*trans* compound and of the *cis* isomers become identical upon iodine catalysis, in light; no *cis*-peak is then shown by the curve since such equilibria contain about 94% of the material in the all-*trans* configuration.

TABLE II

SOME SPECTRAL CHARACTERISTICS OF STEREOISOMERIC DIPHENYLHEXATRIENES IN HEXANE SOLUTION

	Main band			*cis*-Peak	
Steric form	Fine structure	Position of λmax, mμ	Diff. from all-*trans* form at λmax, mμ	$E_{1\,\mathrm{cm.}}^{\mathrm{mol}} \times 10^{-4}$	mμ
All-*trans*	Extensive (Fig. 1)	351	...	None	
cis-I	Moderate (Fig. 2)	349–350	1–2	2.00	268
cis-II	None (Fig. 3)	336–337	14–15	1.40	261–262
cis-III	None (Fig. 4)	334–335	16–17	None	

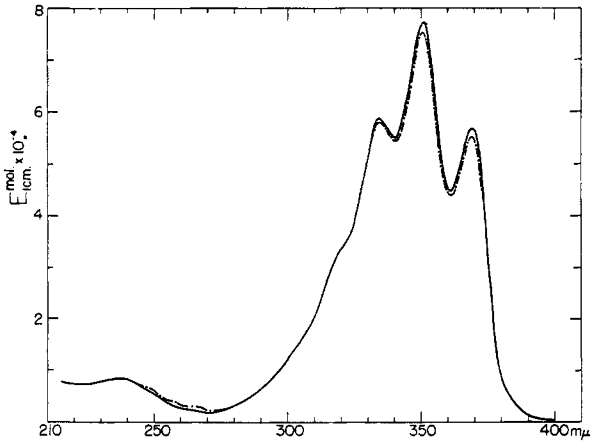

Fig. 1.—Molecular extinction curves of diphenylhexatriene in hexane: —, fresh solution of the all-*trans* form; —·—·, mixture of stereoisomers after 20 min. illumination in the presence of iodine.

We assign the central mono-*cis* configuration (B, Fig. 5) to *cis*-I-diphenylhexatriene on the basis of its high *cis*-peak, the location on the wave length

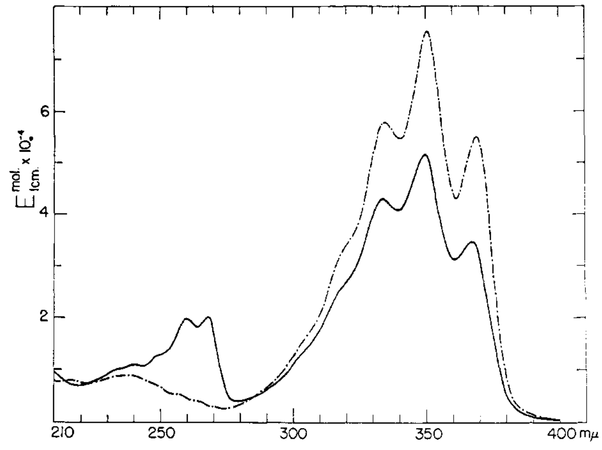

Fig. 2.—Molecular extinction curves of *cis*-I-diphenylhexatriene in hexane: —, fresh solution; —·—·, mixture of stereoisomers after 60 min. illumination in the presence of iodine.

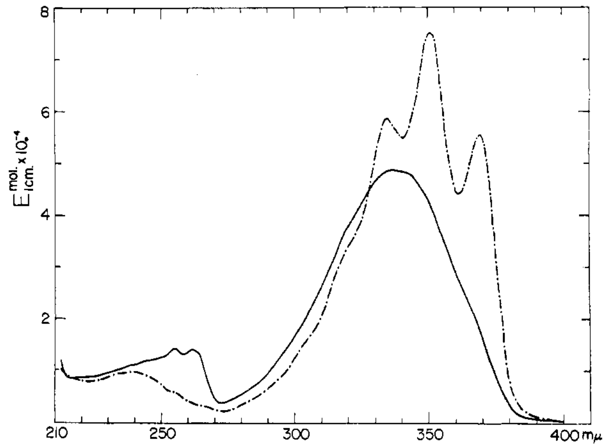

Fig. 3.—Molecular extinction curves of *cis*-II-diphenylhexatriene in hexane: —, fresh solution; —·—·, mixture of stereoisomers after 5 min. illumination in the presence of iodine.

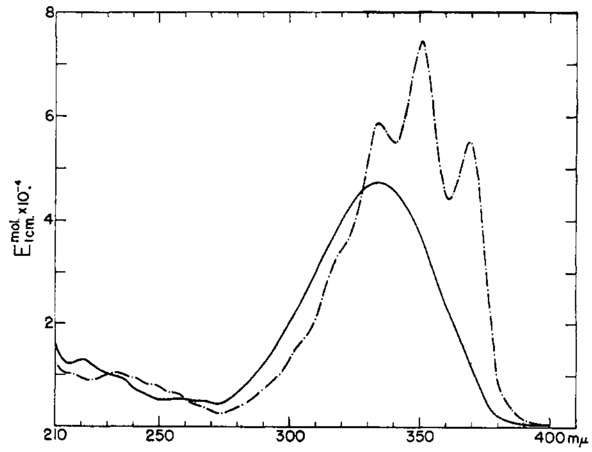

Fig. 4.—Molecular extinction curves of *cis*-III-diphenylhexatriene in hexane: —, fresh solution; —·—·, mixture of stereoisomers after 60 min. illumination in the presence of iodine.

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[7] L. Zechmeister and A. Polgár, THIS JOURNAL, **65**, 1522 (1943); **66**, 137 (1944); L. Zechmeister, A. L. LeRosen, A. W. Schroeder, A. Polgár and L. Pauling, *ibid.*, **65**, 1940 (1943); *cf.* L. Zechmeister, *Chem. Revs.*, **34**, 267 (1944).

scale of its maximum extinction very near that of the all-*trans* maximum, and the extent of the fine structure of the main band. The slightly bent model C (Fig. 5), requiring a sizable but only moderately high *cis*-peak is assigned to the *cis*-II isomer. This assignment is in accordance with the absence of fine structure in the main band and with the shift toward shorter wave lengths, *viz.*, 14–15 mμ, as listed in Table II. The same value was observed earlier in the diphenylbutadiene set for one *trans* → hindered-*cis* rearrangement.[2]

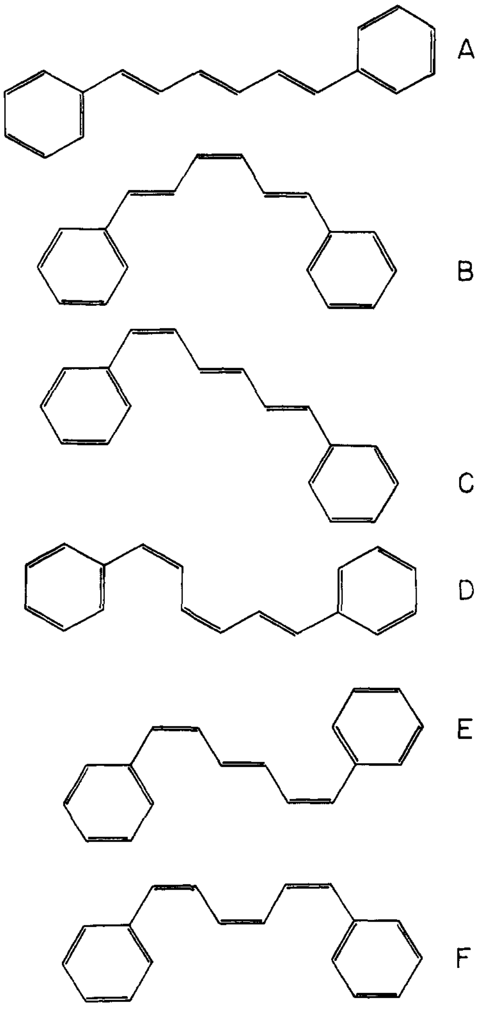

Fig. 5.—Skeleton models of the six theoretically possible *cis–trans*-isomeric diphenylhexatrienes: A, all-*trans*; B, 3-mono-*cis* (configuration assigned to *cis*-I); C, 1-mono-*cis* (assigned to *cis*-II); D, 1,3-di-*cis* (assigned to *cis*-III); E, 1,5-di-*cis*; and F, all-*cis*.

It seems that each of the three remaining configurations (D, E and F, Fig. 5) could *a priori* satisfy the two outstanding features of the *cis*-III spectrum (Fig. 4), *viz.*, the degraded main band and the absence of a *cis*-peak, the latter indicating a straight over-all form of the molecule. The choice, favoring D, has been made on the basis of the following observations.

The speed of the spatial rearrangement in the course of the iodine catalysis (as measured by the change of the extinction value at λ_{max} of the *trans* compound) is sharply dependent on the shape of the diphenylhexatriene molecule. Thus, under the conditions applied, approximately the following times were required for reaching the equilibrium: starting from all-*trans*, 15 min.; from *cis*-II (hindered), 3 min.; and from *cis*-I (unhindered), somewhat surprisingly, 60 min. Evidently, at least in the stereochemical set discussed, a hindered *cis* double bond is much more iodine sensitive than an unhindered one (Fig. 6).

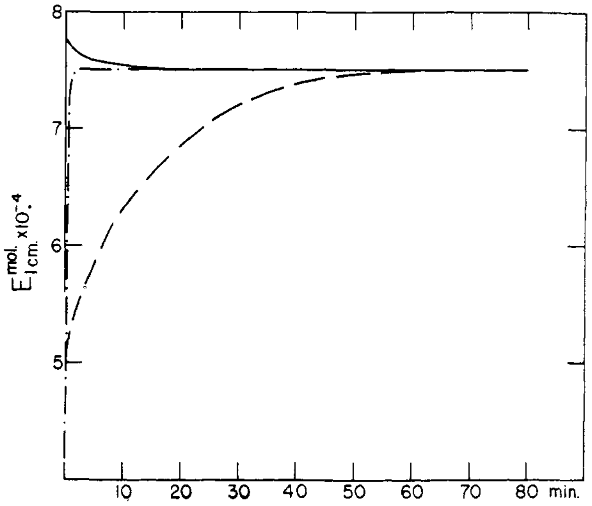

Fig. 6.—Change of the extinction value at 351 mμ (in hexane) during iodine catalysis, in light, starting from the following spatial forms of diphenylhexatriene: —, all-*trans*; -----, *cis*-I; —·—, *cis*-II. Concentrations: 0.2 mg. substance and 2–4 μg. of iodine per 100 ml. Illumination in a 3-ml. quartz cell with ground glass stopper; for further details and the light source *cf.* Materials and Methods.

In a system containing both types of *cis* double bonds it was expected that each of them would show its own degree of iodine sensitivity. Hence, after catalysis, a time–extinction curve would include the following combination of the two individual curves: first, the extinction would rise rap-

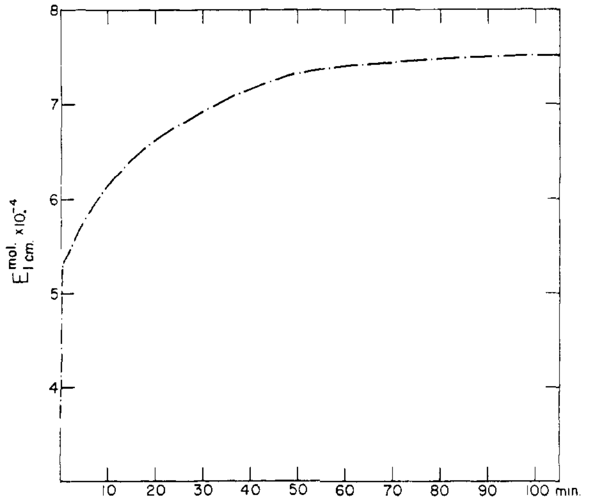

Fig. 7.—Change of the extinction value at 351 mμ (in hexane) during iodine catalysis, in light, of *cis*-III-diphenylhexatriene; for the conditions see legend to Fig. 6.

idly and then, when the *cis* → *trans* rotation of the hindered *cis* double bond had come practically to an end, a much more flattened section of the curve would follow characterizing the rearrangement of the unhindered *cis* double bond. Figure 7 demonstrates that the expected combined curve did appear upon the catalytic treatment of the *cis*-III isomer; the sharp decrease in the slope of the curve was observed within half a minute from the start.

In a parallel experiment the catalytic process was interrupted after 40 sec. by removing the light source, and the solution chromatographed; the main zone, corresponding to 90% of the catalyzed *cis*-III compound was identified as *cis*-I-diphenylhexatriene. Hence, the rearrangement of *cis*-III takes place in two steps; and its molecules must contain the unhindered central double bond and at least one hindered double bond in the *cis* configuration. This eliminates configuration E (that contains a *trans* central double bond) and leaves the choice between D and F.

We propose for *cis*-III-diphenylhexatriene the configuration D, since we believe that F would be far less probable for the following two reasons: 1. The difference in the wave length location of $\lambda_{\max}$ between the all-*trans* isomer and the tri-*cis* form F (as well as E) is expected to exceed considerably the value observed for *cis*-III, *viz.*, 16 mμ in hexane; and 2. As shown in pertinent studies of carotenoid hydrocarbons, there is no tendency for the formation of poly-*cis* compounds in iodine-catalyzed solutions.[8]

The stereoisomeric diphenylhexatrienes (as well as analogous forms of many other polyenes) show individual differences in some regions of their infrared spectra on which we will report elsewhere.

Experimental

Materials 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), and Celite (No. 545, Johns-Manville); a 2:1 mixture of lime ("Sierra, Superfine," U. S. Lime Prod.) and Celite; a 2:1 mixture of silicic acid (Reagent Grade, 100 mesh, Mallinckrodt Chem. Works) and Celite; and a 3:1 mixture of alumina (Merck and Co., Inc., Reagent Grade, ignited) and Celite. Since even some C.P. solvents showed fluorescence in ultraviolet light, they had to be carefully redistilled. "Optical hexane" means hexane (Phillips, Commercial brand) treated repeatedly with fuming sulfuric acid.

The chromatograms were inspected in the light of a portable ultraviolet lamp (Photoflood bulb No. 1; molded Corning light filter No. 5840). Such inspection was carried out rapidly from 1 m. distance; otherwise the chromatographic tube was wrapped in black cloth. All operations should be carried out likewise in darkness or in dim light. Solutions were dried with sodium sulfate and, when necessary, evaporated *in vacuo* (bath, below 35°). Solid and oily preparations were dried in an Abderhalden apparatus (P_2O_5, 1 mm. pressure). The melting points (cor.) refer to an electrically heated Berl block. The photometric readings were taken in a Beckman DU instrument. The mol. extinction coefficients given represent the average of at least two independent experiments. When direct weighings could not be carried out, the concentration of the solution was determined upon iodine catalysis, by reading the extinction of the stereoisomeric equilibrium mixture at $\lambda_{\max}$ and using the mol. extinction coefficient for such mixtures which had been secured by catalyzing the solution of a weighed sample of all-*trans*-diphenylhexatriene. All iodine catalyses were carried out in Pyrex volumetric flasks with illumination, from 60 cm. distance, by two 120-cm. 3500° Mazda lamps (40 watt), white and yellowish.

All-*trans*-diphenylhexatriene was synthesized from cinnamaldehyde, *via* hydrocinnamoin and its dibromide, according to Kuhn and Winterstein,[9] m.p. 203°, $E_{1\,\text{cm}}^{\text{mol}}$ 7.72 × 10^4 at $\lambda_{\max}$ 351 mμ (in hexane).

Anal. Calcd. for $C_{18}H_{14}$: C, 93.05; H, 6.95. Found: C, 92.74; H, 7.12.

Freshly prepared solutions showed only a single fluorescent zone when developed with hexane–acetone 3:1 on a magnesia–lime–Celite column; however, storing dilute solutions in scattered light resulted in a more complex chromatogram.

***cis*-I-Diphenylhexatriene.**—A solution of 200 mg. of the all-*trans* compound in 500 ml. of hexane (in five 100-ml. Pyrex volumetric flasks) was exposed to intense sunshine for 1 hour and concentrated to a total volume of 15 ml., whereby most of the unchanged starting material crystallized out. After filtration these crystals were dissolved in 400 ml. of hexane (25°), then insolated and treated again as described. After a third exposure the solution was not concentrated but combined with the two formerly obtained filtrates (15 + 10 ml.), poured onto a 30 × 7.2 cm. magnesia–lime–Celite column and developed with about 2 l. of benzene–hexane 1:1. A broad fluorescent zone occupied top position; later the (partly separated) zones of *cis*-II (main *cis* zone) and III + IV, migrated downward and reached the filtrate (A, see below). At this point the several centimeters thick, brilliantly fluorescing all-*trans* zone was located in the bottom section, followed by a less than 1 mm. broad interzone and then by the dull-bluish fluorescent *cis*-I zone (1 cm.). The latter zone, still containing some all-*trans* compound, was cut out, eluted with benzene–ethanol 9:1, washed alcohol-free, dried and evaporated completely. The partly crystalline, sticky mass was dissolved in the minimum amount of benzene (25–30°) and precipitated by dropwise addition, with stirring, of 92% methanol while cooling with ice-water. The centrifuged precipitate was dried *in vacuo* for several hours, dissolved in 25–50 ml. of hexane, adsorbed on a 26 × 5.3 cm. column[10] and developed with benzene–hexane 1:1 until the following sequence obtained (the figures on left denote thickness of zones in mm.; fl. = fluorescence or fluorescent):

2	green fl.: destruction products
20	empty interzone
4	blue fl. of medium strength: all-*trans*
30	empty interzone
60	dull bluish fl.: *cis*-I
114	empty section

The *cis*-I zone was cut out and eluted; after the addition of water the epiphase was washed, dried and evaporated. The crystalline residue was transferred into a small centrifuge tube by means of a minimum amount of abs. ethanol and recrystallized by careful addition (with stirring) of 1 vol. of 50% alcohol at room temperature. The centrifuged crystals were washed in the tube with 75% ethanol, centrifuged again and dried at the temperature of boiling acetone for several hours; yield 11 mg. of pale yellow, microscopic needles, m.p. 107°.

Anal. Calcd. for $C_{18}H_{14}$: C, 93.05; H, 6.95. Found: C, 92.55; H, 7.46; $E_{1\,\text{cm}}^{\text{mol}}$ 5.15 × 10^4 at $\lambda_{\max}$ 350 mμ (in hexane).

Upon standing at room temperature in scattered light for a few minutes, the hexane solution of the pure product gave a one-zone chromatogram (*cis*-I except for minute traces). Longer standing caused the appearance of several new fluorescent zones; that of the all-*trans* compound was predominant.

***cis*-II-Diphenylhexatriene.**—Filtrate A (see above, meanwhile kept in deep freeze, in darkness) was evaporated completely. The solution of the oily residue in 100 ml. of hexane was adsorbed on a 30 × 7.2 cm. magnesia–lime–Celite column and developed with benzene–hexane 1:2. A strongly

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(8) *Cf.* L. Zechmeister, *Chem. Revs.*, **34**, 267 (1944); L. Zechmeister and F. J. Petracek, THIS JOURNAL, **74**, 282 (1952).

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

(10) The magnesia–lime–Celite column had been prewashed with 500-ml. portions of benzene–methanol 1:1, then with benzene, and finally with hexane in order to eliminate some impurities contained in the adsorbent that would have prevented the isolation of pure substances.

fluorescent 1-cm. zone of the all-*trans* isomer (formed during the operations) appeared in the top section while a 4-cm. *cis*-II zone, fairly strongly fluorescent, was located near the bottom. The latter zone was not clearly separated by an interzone from the dull grayish-blue fluorescent *cis*-III zone (0.5 cm. thick) but could be cut out on the basis of the different fluorescence shades of the two isomers. At this point the very faintly fluorescent, narrow *cis*-IV zone had reached the filtrate: filtrate B. The *cis*-II and *cis*-III zones were separated from each other as well as possible by careful cutting. Both were eluted with benzene containing a few per cent. abs. alcohol. The *cis*-III eluate was washed, dried and kept in darkness in the deep freeze until further treatment (solution C, see below).

The *cis*-II fraction was treated in a similar manner, then evaporated completely. The oily residue was dissolved in a few milliliters of optical hexane and developed with the same solvent on a 26 × 5.3 cm. silicic acid–Celite column (prewashed successively with 500-ml. portions of acetone–ether 1:1, acetone, and optical hexane):

10 strong blue fl.: all-*trans*
50 empty interzone
80 fairly strong blue fl.: *cis*-II
120 empty section

The main zone was eluted with distilled (non-fluorescent) acetone–hexane 1:1, followed by pure acetone; the eluate was washed, dried and evaporated. The pale yellow oily residue (20 mg.) represented chromatographically homogeneous, pure *cis*-II-diphenylhexatriene, provided that the operations had been carried out in subdued light, at low temperature. Attempts to crystallize such preparations have failed; $E^{\mathrm{mol}}_{1\,\mathrm{cm}} = 4.87 \times 10^4$ at $\lambda_{\max}$ 337 mμ (in hexane; determined after iodine catalysis).

A very similar value, *viz.*, 4.92×10^4 was obtained by direct photometry of a weighed oil sample, although chromatography immediately following the spectral readings already showed the presence of minor amounts of newly formed *trans* compound. The coincidence of the two extinction values mentioned proves the purity of the sample. Longer standing in hexane solution involves far-reaching rearrangement to the *trans* form.

cis-**III-Diphenylhexatriene**.—The evaporation residue of solution C (see above) was dissolved in a few milliliters of hexane and adsorbed on a 20 × 4.2 cm. magnesia–lime–Celite column (prewashed with 250-ml. portions of methanol–benzene 1:1, benzene, and hexane). Upon developing with benzene–hexane 1:6 the chromatograms included a narrow, fairly strongly fluorescent *cis*-II zone and, below it, the broader, well-separated, dull-fluorescent zone of the *cis*-III isomer. The latter was eluted with hexane containing a few per cent. methanol, and after washing and drying, evaporated. Although the hexane solution of the residue showed only a single fluorescent zone on the column, the presence of a colorless, non-fluorescent contaminant was indicated by the spectra (strong extinction in the region, 200–300 mμ). This impurity could be eliminated by rechromatography on alumina–Celite (20 × 3.3 cm., prewashed as mentioned above; developer, hexane). After elution with pure benzene and total evaporation, the residue was evaporated with 2 × 2 ml. of hexane. The residue (less than 1 mg.) was chromatographically homogeneous and spectroscopically pure. The following mol. extinction coefficient of *cis*-III was secured *via* the iodine catalysis method; $E^{\mathrm{mol}}_{1\,\mathrm{cm}} = 4.73 \times 10^4$ at $\lambda_{\max}$ 334–335 mμ (in hexane).

The catalyzed solution gave practically the same chromatogram as obtained by catalyzing the all-*trans* form. The all-*trans* isomer prepared from *cis*-III was identified in a mixed chromatogram test.

cis-III-Diphenylhexatriene solutions undergo far-reaching stereoisomerization when kept at room temperature, in darkness, for a few days. Subsequent chromatography then shows the presence of a minor isomer (probably *cis*-II) and a much broader all-*trans* zone, both located above unchanged *cis*-III.

cis-**IV-Diphenylhexatriene**.—Filtrate B (see above) contained small amounts of very labile *cis*-IV isomer that was much less strongly adsorbed than the three other *cis* forms. Its spectrum was distorted by the presence of a contaminant (absorbing in the region, 200–300 mμ, in hexane) which could not be eliminated by changing the adsorbing system. However, iodine catalysis converted the section of the spectral curve above 325 mμ, into that obtainable by catalysis of the all-*trans* form. Spontaneous stereoisomerization of *cis*-IV solutions, at 4°, in darkness, yielded the *cis*-II and all-*trans* isomers.

Composition and Resolution of Stereoisomeric Mixtures (*cf.* also Table I). (a) **Iodine Catalysis**.—A solution of 1.50 mg. of all-*trans*-diphenylhexatriene in 50 ml. of hexane was illuminated with a daylight lamp in the presence of 20 μg. of the catalyst for 45 min. and developed with the same solvent on a 30 × 3.2 cm. lime–Celite column:

2 bluish fl.: destruction products
54 empty interzone
45 strong blue fl.: unchanged all-*trans*
3 empty interzone
11 weak blue fl.: *cis*-I
38 empty interzone
60 weak greenish-blue fl.: *cis*-II
87 empty section
Filtrate: weak fl.: *cis*-III and *cis*-IV

After elution with hexane + 5% abs. alcohol the individual isomers were transferred into hexane and estimated photometrically. The respective wave length positions of $\lambda_{\max}$ were those mentioned in Table II.

When a solution of 0.1 mg. of *cis*-III in 50 ml. of hexane was illuminated in the presence of 1–2 μg. of iodine for 40 sec. and developed with the same solvent on a 20 × 3.2 cm. alumina–Celite column, the following sequence was observed (starting material = 100%):

10 weak blue fl.: all-*trans* (few %)
10 empty interzone
20 relatively strong blue fl.: *cis*-I (90%)
10 empty interzone
30 faint greenish-blue fl.: unchanged *cis*-III (few %)
120 empty section

(b) **Insolation**.—The solution (0.75 mg. of all-*trans* form in 25 ml. of hexane; Pyrex volumetric flask) was exposed to fairly intense sunshine for 60 min. (temperature, 25° → 32°) and developed on a 30 × 3.2 cm. lime–Celite column:

10 empty section
2 greenish fl.: destruction products
50 empty interzone
40 strong blue fl.: unchanged all-*trans*
12 empty interzone
14 blue fl.: *cis*-I
70 empty interzone
30 weak greenish-blue fl.: *cis*-II
72 empty section
Filtrate: weak bluish fl.: *cis*-III + *cis*-IV (traces)

The further operations were carried out as under (a).

(c) **Refluxing** of dilute *n*-propyl alcohol solutions of the all-*trans* isomer in dim light for 45 min. did not result in the appearance of *cis* zones in the chromatogram, except perhaps for traces. A similar degree of thermostability was shown by dilute *cis*-II solutions in boiling hexane. In contrast, when a hexane solution of *cis*-I had been refluxed for 30 min., subsequent chromatography showed, above the unchanged *cis*-I fraction, an all-*trans* zone, corresponding to 4% of the starting material. Approximately the same extent of isomerization was reached at 25° in 3 days.

(d) **Melting Crystals**.—A sample of 2.5 mg. of all-*trans*-diphenylhexatriene was sealed *in vacuo* in a small glass tube and immersed in a boiling diphenyl ether bath (b.p. 259°) in darkness, for 15 min. The tube was cooled with ice-water, crushed and extracted first with 3 × 5 ml. of hexane (20°) in order to dissolve most of the *cis* isomers formed, and then with 3 × 5 ml. of boiling hexane that took up the unchanged portion of the *trans* compound. The combined extract was developed with hexane on a 30 × 3.2 cm. lime–Celite column:

2 bluish fl.: destruction products
55 empty interzone
35 strong blue fl.: unchanged all-*trans*
18 empty interzone
12 dull blue fl.: *cis*-I
60 empty interzone
35 dull greenish-blue fl.: *cis*-II
83 empty section

(e) **Stereoisomerization *via* the BF_3 Complex.**—A solution of 10 mg. of the all-*trans* compound in 50 ml. of hexane was shaken mechanically, in darkness, with 2 ml. of distilled boron trifluoride etherate for 10 min. Then the hypophase was light brown, indicating the presence of a complex. The latter was broken up immediately by intense shaking with 10 ml. of 95% methanol for 1–2 min. The colorless hexane solution was washed methanol-free, dried and evaporated completely. The residue was dissolved in 100 ml. of hexane and 25 ml. of this solution was developed with the same solvent on a 35 × 3.7 cm. lime–Celite column until the following sequence obtained:

67	empty section
80	strong blue fl.: unchanged all-*trans*
2	empty interzone
6	fairly strong blue fl.: *cis*-I
35	empty interzone
17	weak greenish-blue fl.: *cis*-II
25	empty interzone
23	very weak bluish fl.: *cis*-III
55	empty interzone
40	very faint bluish fl.: destruction products

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The Friedel–Crafts Reaction with Trimethylene Oxide and *n*-Propyl Ether

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RECEIVED AUGUST 10, 1953

Trimethylene oxide condenses with benzene and with mesitylene in the presence of aluminum chloride to form 50–70% yields of the 3-hydroxypropyl derivative. Both in ease of reaction and lack of isomerization of the entering group, the Friedel–Crafts alkylation with this cyclic ether differs markedly from that with acyclic ethers. The reaction of *n*-propyl ether with benzene has been studied for comparison.

The Friedel–Crafts alkylation of aromatic hydrocarbons and phenols with ethers is a well-established reaction,[2] the best known example of which is probably the aluminum chloride-catalyzed reaction of benzene with ethylene oxide to give 2-phenylethanol. The reaction of trimethylene oxide with aromatic compounds was reported several years ago by Thiemer,[3] but no information is available regarding the reaction conditions required, the hydrocarbons used, or the structures of the products obtained, except that they were primary alcohols. Primary alcohols, however, might be obtained by introduction of either the 3-hydroxypropyl or the 2-hydroxy-1-methylethyl group on the aromatic ring. The course of this reaction is of interest in connection with other aspects of the chemistry of four-membered cyclic ethers.[4]

In the present work the reaction of trimethylene oxide with benzene and with mesitylene has been carried out under conditions similar to those usually employed for the ethylene oxide reaction, except for a longer reaction time or higher temperature. The products were 3-phenyl-1-propanol and 3-mesityl-1-propanol, isolated in 50–70% yields. In neither case was there evidence for any other aromatic alcohol being formed, and the infrared spectrum of the benzene product was identical to that of authentic 3-phenyl-1-propanol. The purity of the products and the directness of the method attaches preparative value to the reaction, especially for compounds like 3-mesityl-1-propanol.[5]

In contrast to the earlier report,[3] trimethylene oxide was found to react at a considerably slower rate than ethylene oxide, as shown by an experiment in which an equimolar mixture of both oxides was allowed to react simultaneously with benzene. When the reaction was quenched after a relatively short time, 2-phenylethanol was the only product detectable. The use of boron trifluoride as a catalyst was unsuccessful, even at 0–10°, as it brought about polymerization of trimethylene oxide instead of alkylation.

The complete lack of isomerization of an entering primary group is unusual in a Friedel–Crafts alkylation.[6] A possible reason might be that the ether function, like the hydroxyl function in normal alcohols could cause the aluminum chloride-catalyzed alkylation to occur predominately by a displacement-type mechanism which avoids rearrangement.[7] Since the published examples of aluminum chloride-catalyzed alkylations with *n*-alkyl ethers have not involved alkyl groups that would be likely to isomerize,[8] the reaction of benzene with *n*-propyl ether was investigated here. This ether was selected because it is the simplest one capable of giving isomeric alkylbenzenes and because the length of the carbon chain is the same as in trimethylene oxide.

The reaction was carried out in the usual manner for acyclic ethers, except for the use of a shorter

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[2] A portion is reviewed by C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, N. Y., 1941.

[3] E. T. Theimer, U. S. Patent 2,125,968 (1938), and Abstracts, Division of Organic Chemistry, 99th Meeting of the American Chemical Society, Cincinnati, Ohio, April, 1940, p. 42.

[4] S. Searles, THIS JOURNAL, **73**, 124, 4515 (1951); S. Searles and M. Tamres, *ibid.*, **73**, 3704 (1951); S. Searles and C. F. Butler, *ibid.*, **76**, 56 (1954).

[5] The previous preparation by J. Sordes, *Compt. rend.*, **195**, 247 (1932), required five steps.

[6] (a) V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940); (b) H. Pines, L. Schmerling and V. N. Ipatieff, THIS JOURNAL, **62**, 2901 (1940).

[7] Such a mechanism has been discussed by H. C. Brown, *et al.*, *Ind. Eng. Chem.*, **45**, 1462 (1953).

[8] For example, J. F. Norris and B. M. Sturgis, THIS JOURNAL, **61**, 1413 (1939); P. E. Malson and J. H. Gardner, Abstracts, Division of Organic Chemistry, 97th Meeting of the American Chemical Society, Baltimore, 1939, p. 35. An unpublished thesis by R. F. Prindle (Ph.D. Thesis, Washington University, St. Louis, Mo., June, 1942) states that *sec*-butylbenzene was the only product (16% yield) obtained from the reaction of *n*-butyl ether, benzene and aluminum chloride, but since he did not have an efficient fractionating method or an infrared spectrum of the product, the formation of *n*-butylbenzene cannot be excluded. This would seem likely in view of his observation that *t*-butyl isopropyl ether alkylated benzene in the presence of aluminum chloride to give predominantly isopropylbenzene, contrary to carbonium ion theory.