zone precipitated continuously during the reaction. It was recrystallized from dimethylformamide.

**Phenanthrene Ozonide.**—The ozonide was obtained in 85% yield by pouring the acetic acid solution into very cold water. Infrequently the white colloid that first formed failed to agglutinate to yield the granular product. Vacuum removal of some of the solvent avoided this difficulty. All attempts to remove all the water from the product obtained in this way failed. However, a dry product was obtained from the chloroform solution. Most of the solvent was removed under vacuum. The concentrate was poured into absolute methanol which had been cooled in a Dry Ice-bath and the precipitate was filtered immediately, washed with more cold methanol and dried in a vacuum desiccator.

The precipitated ozonide is a white, amorphous powder that easily acquires a static charge. It burns fiercely, but is stable to shock. It softens and melts (65–90°) like a glass and, unlike most ozonides, is soluble in cold ether. Once precipitated it is stable in water and dilute acid suspension for weeks, but it decomposes in dry air.

The infrared spectra of the ozonide from chloroform and from acetic acid are essentially superimposable.

*Anal.* Calcd. for $C_{14}H_{10}O_3$: C, 73.33; H, 4.46; mol. wt., 226. Found: C, 73.34; H, 4.61; mol. wt. (Rast using *dl*-camphor), 223.

**Ozonide Decomposition. (a) Catalytic Reduction.**—Using the method of Fisher[22] but at room temperature, the theoretical amount of hydrogen was absorbed. A quantitative determination of the biphenyl-2,2′-dialdehyde thus formed[23] showed a yield of 57.5%. This low yield is understandable in the light of Fisher's experience.[22]

**(b) Hydrolysis to Biphenyl-2,2′-dialdehyde.**—The acetic acid solution of the ozonide was poured into four times its volume of water and the resulting colloid was let stand for two days. At the end of that time a 51% yield of the aldehyde was filtered off; m.p. 60–61°. The derivatives listed in Table I were prepared in the usual way. The *p*-nitrophenylhydrazone was purified by chromatography in a dioxane solution on activated alumina. The column was developed with 10% ethanol in dioxane, extruded and sectioned. The lower dark red band was eluted with hot dioxane and the material recrystallized from dioxane–water.

**(c) Oxidation to 2,2′-Diphenic Acid.**—The filtrate from the above preparation of the dialdehyde gave, on warming with potassium permanganate, a 25.5% yield of diphenic acid, m.p. 229–230°. The ozonide itself was oxidized with alkaline permanganate in the cold to an acid, m.p. 229–231°; mixed m.p. with an authentic sample of diphenic acid 229–231°; *p*-nitrobenzyl ester m.p. 184–185° (183°).[24]

**Alternate Preparation of 2,2′-Biphenyldialdehyde Bis-(2,4-dinitrophenylhydrazone).**—The method of Weygand[11] was used; m.p. of this 2,4-dinitrophenylhydrazone 290°; mixed m.p. with product from ozonolysis 290°. For this synthesis the N,N′-diphenyl-N,N′-dimethyl-2,2′-biphenamide was prepared according to the method of Rapson and Shuttleworth.[25] The product melted at 166–167° compared to the 160–162° reported by Weygand.

*Anal.* Calcd. for $C_{28}H_{24}N_2O_2$: C, 79.97; H, 5.75. Found: C, 80.06; H, 5.65.

**Glyoxal Determination.**—A stock solution was prepared as follows. To 2 ml. of sulfuric acid and 0.8 g. of 2,4-dinitrophenylhydrazine was gradually added 8 ml. of water. To this solution were added 50 ml. of acetic acid and 11 ml. of water. Test-tubes were prepared with 2 ml. of the stock solution diluted with 2 ml. of water. The mixture to be tested was distilled, 2 ml. of the distillate being run directly into the test-tube. Usually three samples were taken. Eleven ml. of water then was added and the mixture heated to boiling. If glyoxal were present the solution became cloudy almost immediately. On standing a flocculent precipitate formed and floated to the top as a large orange ball. The dry weight of this apparently large mass was negligible. In the control experiments the m.p. agreed with the literature value of 328° for the glyoxal derivative.

For the actual test on phenanthrene ozonide, the ozonolysis mixture was first reduced catalytically as noted above, and then directly distilled into the test-tubes. No precipitate was formed.

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[22] F. G. Fisher, H. Dull and L. Ertel, *Ber.*, **65**, 1467 (1932).

[23] H. A. Iddles, A. W. Low, B. D. Rosen and R. T. Hart, *Ind. Eng. Chem., Anal. Ed.*, **11**, 102 (1939).

[24] T. L. Kelly and M. Segura, THIS JOURNAL, **56**, 2497 (1934).

[25] W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 487 (1941).

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[CONTRIBUTION NO. 1990 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

# On the *cis* Forms of Some Biphenylene Derivatives of Butadiene and Hexatriene

BY EUGENE F. MAGOON AND L. ZECHMEISTER

RECEIVED MAY 26, 1955

All theoretically possible *cis* forms of 1,6-di-biphenylenehexatriene, 1-biphenylene-4-phenylbutadiene and 1-biphenylene-6-phenylhexatriene were prepared. They were characterized on the basis of their chromatographic and spectroscopic behavior as well as of their relative stabilities. The observations were in general agreement with those made in the series of $\alpha,\omega$-diphenyl-polyenes and symmetrical polyene-azines.

In the present paper we describe the stereochemical behavior of three compounds so far known only in the *trans* form. They are characterized by bulky end groups attached to short unsaturated systems. Di-biphenylenehexatriene has been selected because its only *cis* isomer represents a sterically "unhindered" type (Fig. 1), whereas biphenylenephenylbutadiene yields a "hindered" *cis* form (Fig. 2). Finally, biphenylenephenylhexatriene may assume the *cis* configurations B-D (Fig. 3), including a hindered mono*cis*, an unhindered mono*cis* and a hindered-unhindered di*cis* isomer. As observed earlier in the $\alpha,\omega$-diphenylpolyene[1] and symmetrical polyene-azine[2] series, when a terminal double bond of the open chain undergoes *trans* → *cis* rearrangement, a spatial conflict arises between a hydrogen atom of the side-chain and a ring hydrogen, with the result that the *cis* compound thus formed shows a considerably degraded spectrum. In contrast, an unhindered *cis* double bond involves a relatively slight change in the all-*trans* spectral curve.

We have now observed that the three *trans* compounds mentioned which are easily synthesized according to Kuhn and Winterstein,[3] can be rearranged to yield all expected *cis* forms (Figs. 1–3)

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[1] A. Sandoval and L. Zechmeister, THIS JOURNAL, **69**, 553 (1947); J. H. Pinckard, B. Wille and L. Zechmeister, *ibid.*, **70**, 1937 (1948); K. Lunde and L. Zechmeister, *ibid.*, **76**, 2308 (1954); L. Zechmeister and A. L. LeRosen, *ibid.*, **64**, 2755 (1942); L. Zechmeister and J. H. Pinckard, *ibid.*, **76**, 4144 (1954); *cf.* L. Zechmeister, *Experientia*, **10**, 1 (1954).

[2] J. Dale and L. Zechmeister, THIS JOURNAL, **75**, 2379 (1953).

[3] R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 116 (1927).

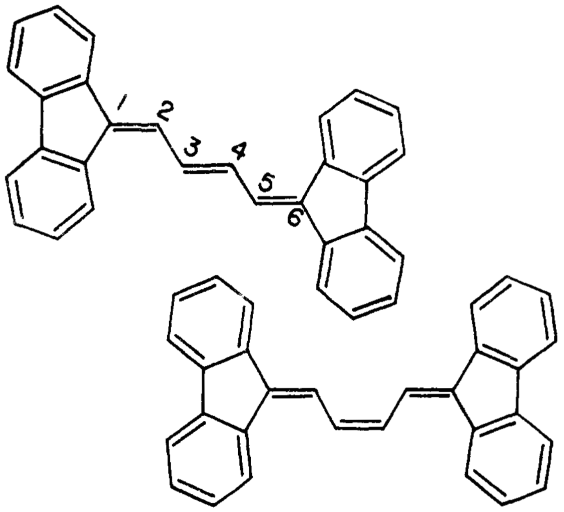

Fig. 1.—Skeleton models of the two stereoisomeric dibiphenylenehexatrienes: top, *trans;* bottom, 3-*cis*.

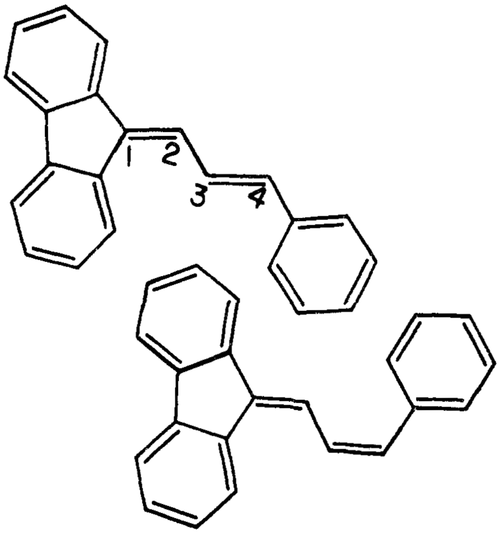

Fig. 2.—Skeleton models of the two stereoisomeric biphenylenephenylbutadienes: top, *trans;* bottom, 3-*cis*.

when submitted to some reversible thermic or photochemical treatments. The zones of the chromatographically separated individual isomers are best observed in ultraviolet light. All *cis* forms appeared below the corresponding *trans* zone, and this weakening of the adsorption affinity was especially marked in the presence of a hindered *cis* double bond. Iodine-catalyzed equilibria contained 93–98% *trans* form in agreement with some data obtained in the diphenylpolyene series. For preparative purposes a brief fusion of *trans* crystals was the preferred procedure.

As expected, no *cis* peaks[4] appeared in the spectral curves, since *trans* → *cis* rearrangements do not alter the straight over-all shape of the aliphatic conjugated system in this type of compound.

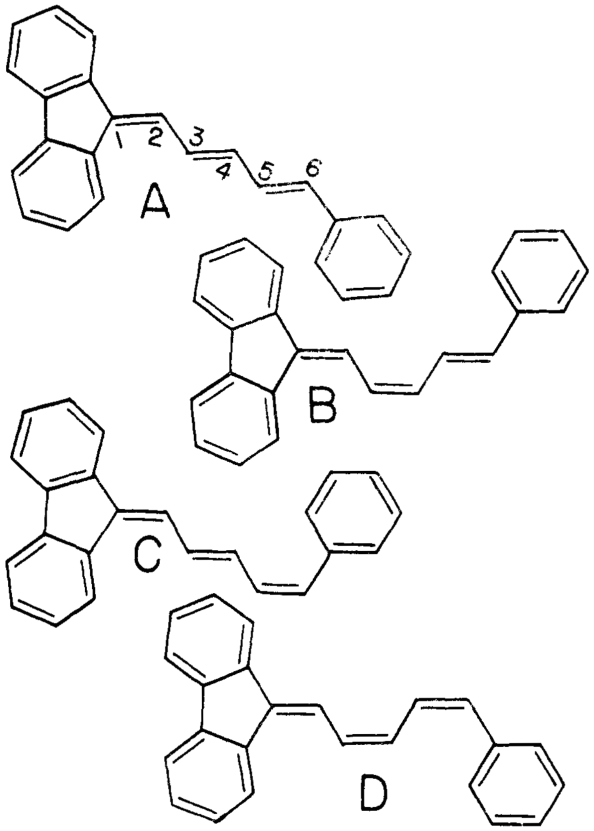

Fig. 3.—Skeleton models of the four stereoisomeric biphenylenephenylhexatrienes: A, all-*trans;* B, 3-mono*cis* (configuration assigned to "*cis*-I"); C, 5-mono*cis* (assigned to "*cis*-II"); and D, 3,5-di-*cis* (assigned to "*cis*-III").

**1,6-Di-biphenylenehexatriene** yielded a crystalline *cis* form. As shown in Fig. 4 this *trans* → *cis* rearrangement caused a relatively slight decrease in the fine structure of the main band and only a slight shift of the maxima toward shorter wave lengths.

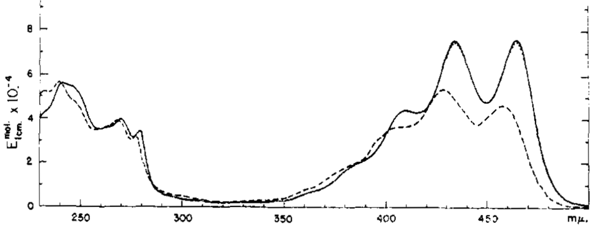

Fig. 4.—Molecular extinction curves of di-biphenylenehexatrienes (in cyclohexane): ——, fresh solution of the *trans* form; ------, fresh solution of the *cis* form; and ...., mixture of the stereoisomers after iodine catalysis (the dotted line differs from the full line only in the region of the main maxima).

**1-Biphenylene-4-phenylbutadiene** gave an oily *cis* isomer whose main spectral band was void of fine structure (Fig. 5). In the absence of solvents this relatively labile isomer rearranged, even in darkness, to give the crystalline *trans* form. Its behavior is analogous to that of mono*cis*-diphenylbutadiene.[1]

**1-Biphenylene-6-phenylhexatriene** was converted into the three expected crystalline *cis*

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[4] 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).

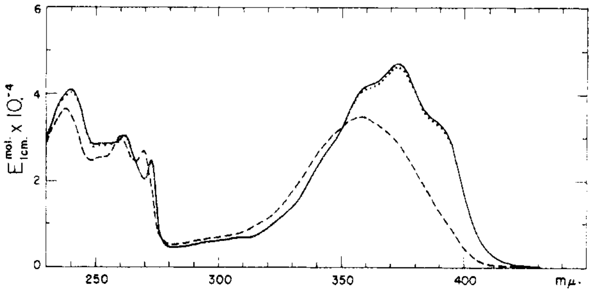

Fig. 5.—Molecular extinction curves of biphenylenephenylbutadienes (in hexane): ——, fresh solution of the *trans* form; ------, fresh solution of the *cis* form; and . . . . , mixture of the stereoisomers after iodine catalysis.

forms, termed, in the order of decreasing adsorption affinities, *cis*-I, II and III. Their configurations have been established as follows. The main spectral band of *cis*-I showed a considerable degree of fine structure and, furthermore, only a slight difference in the position of its maxima from that of the *trans* form. It clearly represents the only possible unhindered *cis* member of this set, *i.e.*, the 3-mono*cis* isomer (B, Fig. 6). The *cis*-II and III are hindered forms, and no fine structure appears in their curves. Considering the larger shift in the position of the maxima and the lower extinction values, we have assigned to *cis*-III the 3,5-di*cis* configuration (D, Fig. 6); this leaves the 5-mono*cis* configuration (C) for *cis*-II.

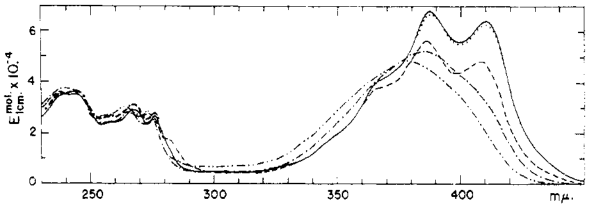

Fig. 6.—Molecular extinction curves of biphenylenephenylhexatrienes (in hexane): ——, fresh solution of the all-*trans* form; ------, fresh solution of 3-mono*cis* ("*cis*-I"); –·–·–, fresh solution of 5-mono*cis* ("cis-II"); –··–··–, fresh solution of 3,5-di-*cis* ("*cis*-III"); and . . . . , mixture of the stereoisomers after iodine catalysis.

The latter assignments have been confirmed in the following manner. Upon iodine catalysis of *cis*-III under unusually mild conditions and subsequent chromatography the recovered stereoisomeric mixture was found to be composed of *cis*-I to the extent of 80%. As had been pointed out by Lunde and one of the writers, hindered *cis* double bonds respond to iodine catalysis much more rapidly than do unhindered such bonds. In the present instance the process may be formulated as: 3,5-di*cis* → 3-mono*cis* → all-*trans*. The hindered 5-mono*cis* form did not appear in such experiments, and we obtained it exclusively from the all-*trans* compound.

With respect to relative stabilities the following statements valid for the three sets can be made (Tables I–III). Under the conditions of refluxing in darkness the *trans* and *cis* configurations are practically equally resistant. However, the *cis* forms, especially the hindered ones, are markedly more photo-sensitive than the corresponding *trans* compound. With reference to the melting points it was noted that unhindered *cis* forms melted somewhat higher but hindered ones considerably lower than the (all-)*trans* isomer.

## Experimental

**Materials and Methods.**—The following adsorbents were used: a 2:1 mixture of lime (Sierra, Superfine, U. S. Lime Prod.) and Celite (No. 545, Johns-Manville), a 3:1:1 mixture of alumina (Alcoa −80 mesh, reground to −200 mesh), lime and Celite, a 3:1 mixture of magnesia (Seasorb 43, Food, Mach., and Chem. Corp.) and Celite, and a 3:1:1 mixture of magnesia, lime and Celite.

As an ultraviolet light source a Photoflood bulb No. 1 was used, equipped with a molded Corning light filter No. 5840. Photoisomerizations were effected using the same bulb without the filter. Iodine catalyses (iodine = 1–2% of the substance) were carried out by illuminating with two 120-cm. long 3500° Mazda lamps (40 watt; white and yellowish). The mol. extinction coefficients given represent the average of at least two independent experiments. When direct weighings were not possible, the concentrations were determined upon iodine catalysis, and for the calculations the extinction coefficient of the resulting equilibrium mixture was used as known from a parallel experiment with a weighed *trans* sample.

Photometric readings were taken on fresh solutions with a Cary recording spectrophotometer, model 11M, using optical grades of solvents. Solvents were removed *in vacuo*. Melting of crystals was carried out in a brass block, while the melting points (cor.) refer to an electrically heated Berl block.

The ratios of the isomers in the various stereoisomeric mixtures of di-biphenylenehexatriene and biphenylenephenylbutadiene were determined from spectral data of the mixtures with the aid of Fig. 7.

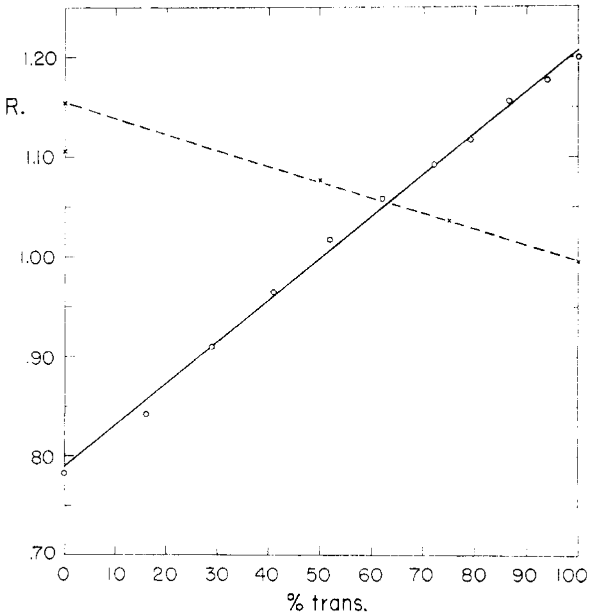

Fig. 7.—Full line, biphenylenephenylbutadiene; dependence of the ratio $R$, extinction at 375 m$\mu$/extinction at 358 m$\mu$ (in hexane) on the composition of artificial mixtures of the *cis* and *trans* forms. Dashed line, di-biphenylenehexatriene; dependence of the ratio, extinction at maximum in the range 428–434 m$\mu$/extinction at maximum in the range 458–465 m$\mu$ (in cyclohexane) on the composition of artificial mixtures of the *cis* and *trans* forms.

Microanalyses were carried out by Mr. G. A. Swinehart in Dr. A. J. Haagen-Smit's laboratory.

***trans*-Di-biphenylenehexatriene** (*Cf.* Table I).—The brownish condensation product from fluorenone and dihydromuconic acid was purified on lime–Celite (developer, benzene) which eliminated a blue top zone. The crystals thus obtained were red-orange and melted at 331.5–333°; $E^{\text{mol}}_{1\,\text{cm.}}$ 7.65 × 10⁴ at $\lambda_{\max}$ 465 mμ (in cyclohexane).

*Anal.* Calcd. for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 94.30; H, 5.82.

TABLE I

RATIO OF THE *trans* AND *cis* FORMS IN STEREOISOMERIC MIXTURES OF DI-BIPHENYLENEHEXATRIENES

| Steric form treated | Treatment | Ratio, *trans*:*cis* in-recov. subst. | Loss (% of starting material) |
|---|---|---|---|
| *trans* | Iodine cat.[a] | 96:4 | 0 |
| *trans* | Irradiation[b] | 90:10 | 0 |
| *trans* | Refluxing[c] | No effect | |
| *trans* | Heating soln.[d] | 83:17 | 1 |
| *trans* | Melting cryst.[e] | 84:16 | 26 |
| *cis* | Iodine cat.[f] | 97:3 | 20 |
| *cis* | Iodine cat.[g] | 90:10 | 11 |
| *cis* | Irradiation[h] | 81:19 | 12 |
| *cis* | Insolation[i] | 97:3 | 14 |
| *cis* | Refluxing[c] | No effect | |
| *cis* | Heating soln.[d] | 86:14 | No estim. |
| *cis* | Melting cryst.[e] | 57:43 | No estim. |

[a] 15 min. at 60 cm. from light source (quartz cell). [b] 20 min. at 10 cm. from Photoflood bulb (quartz). [c] Cyclohexane solution refluxed in the dark for 60 min. [d] Diphenyl ether solution; 200°, 15 min. (oil-bath). [e] Kept for 5 sec. just above the m.p. [f] 20 min. at 60 cm. from light source (quartz). [g] 3 min. at 60 cm. from light source (quartz). [h] 60 min. at 10 cm. from Photoflood bulb (Pyrex flask). [i] 20 min. in intense sunlight (quartz).

*cis*-**Di-biphenylenehexatriene.**—Ten mg. of the *trans* compound was melted in an evacuated tube for 10 sec. and cooled immediately in an ice-bath. After dissolving the substance in the minimum amount of benzene, 0.5 vol. of hexane was added, and the solution chromatographed (50 × 4.5 cm.; alumina–lime–Celite; benzene) (the figures on the left denote thickness of zones in mm.; the colors were observed in ultraviolet light):

| | |
|---|---|
| 310 | empty section |
| 110 | dark red (*trans*) |
| 37 | pale red (*cis*) |
| 43 | empty section |

The *cis* zone was cut out and eluted with benzene + 10% alcohol, then washed alcohol-free and dried. On removal of the benzene orange-colored crystals appeared that were taken up in the minimum amount of benzene, diluted with 1 vol. of hexane and developed with benzene on lime–Celite (30 × 2.5 cm.):

| | |
|---|---|
| 30 | empty section |
| 25 | red (*trans*) |
| 15 | interzone |
| 35 | pale red (*cis*) |
| 195 | empty section |

The 35-mm. zone yielded, upon recrystallization from hot benzene, 0.6 mg. of the *cis* form, m.p. 333–335°, $E^{\text{mol}}_{1\,\text{cm.}}$ 5.44 × 10⁴ at $\lambda_{\max}$ 458.5 mμ (in cyclohexane). In all 8 mg. of pure crystals were obtained.

*Anal.* Calcd. for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 95.19; H, 5.17.

*trans*-**Biphenylenephenylbutadiene** (*Cf.* Table II).—Recrystallization from chloroform yielded fine yellow needles which were chromatographically pure (magnesia–Celite; benzene), m.p. 150.5–151°; $E^{\text{mol}}_{1\,\text{cm.}}$ 4.7 × 10⁴ at $\lambda_{\max}$ 373 mμ (in hexane).

*Anal.* Calcd. for $C_{22}H_{16}$: C, 94.24; H, 5.76. Found: C, 94.33; H, 5.86.

TABLE II

RATIO OF THE *trans* AND *cis* FORMS IN STEREOISOMERIC MIXTURES OF BIPHENYLENEPHENYLBUTADIENES

| Steric form treated | Treatment | Ratio, *trans*:*cis* in recov. subst. | Loss (% of starting material) |
|---|---|---|---|
| *trans* | Iodine cat.[a] | 98.5:1.5 | 11 |
| *trans* | Irradiation[b] | No effect | |
| *trans* | Insolation[c] | No effect | |
| *trans* | Heating soln.[d] | No effect | |
| *trans* | Melting cryst.[e] | 90:10 | 19 |
| *cis* | Iodine cat.[f] | 98:2 | 1 |
| *cis* | Irradiation[g] | 81:19 | 1 |
| *cis* | Insolation[h] | 96:4 | 1 |
| *cis* | Refluxing[i] | No effect | |

[a] 1 min. at 60 cm. from light source (Pyrex flask). [b] 15 min. at 5 cm. from Photoflood bulb (Pyrex). [c] Intense sunlight for 2 hr. (Pyrex). [d] Naphthalene solution heated for 20 min. at 140° (oil-bath). [e] 70 sec. at 345°. [f] 4 min. at 200 cm. from light source (quartz); concn. much lower than in ref. *a*. [g] 90 min. at 15 cm. from Photoflood bulb. [h] Intense sunlight for 5 min. (quartz). [i] Hexane solution refluxed in the dark for 30 min.

*cis*-**Biphenylenephenylbutadiene.**—After melting 500 mg. of the *trans* form in an evacuated tube at 345° for 75 sec., the tube was cooled rapidly, the contents were dissolved in the minimum amount of benzene and developed with the same solvent on a 30 × 7.5 cm. magnesia–Celite column:

| | |
|---|---|
| 2 | yellow |
| 5 | interzone |
| 44 | dark red (*trans*) |
| 94 | interzone |
| 40 | pale red (*cis*) |
| 27 | pale blue |
| 88 | empty section |

The *cis* zone was eluted with benzene + 10% alcohol, the alcohol was washed out and after drying the solvent removed. The oily residue, combined with that from a 200-mg. experiment, was dissolved in benzene + hexane (1:1) and developed with a 3:1 mixture on magnesia–lime–Celite (35 × 3.3 cm.):

| | |
|---|---|
| 5 | yellow |
| 18 | interzone |
| 25 | dark red (*trans*) |
| 38 | interzone |
| 10 | blue |
| 50 | interzone |
| 107 | pale red (*cis*) |
| 25 | pale blue |
| 72 | empty section |

We obtained from the 107-mm. zone 72 mg. of the yellowish, oily *cis* compound. Its solutions were fairly stable in darkness. The concentrations were determined upon iodine catalysis. $E^{\text{mol}}_{1\,\text{cm.}}$ 3.46 × 10⁴ at $\lambda_{\max}$ 357.5 mμ( in hexane). In the absence of solvents, however, crystals of the *trans* compound started to appear within a few hours, even at 20°, in darkness. Hence, in the time necessary for drying an analytical sample almost complete isomerization was unavoidable and the first of the following analyses refers to such a mixture; for the second one a sample was recrystallized from ethanol.

*Anal.* Calcd. for $C_{22}H_{16}$: C, 94.24; H, 5.76. Found: C, 94.52, 94.23; H, 5.45, 5.70.

**All-*trans*-biphenylenephenylhexatriene** (*Cf.* Table III).—The phenylpentadienal (which was then condensed with fluorene) was prepared according to Jones, *et al.*[5] Several minor contaminants were eliminated from the product by chromatographing on magnesia–Celite. Large yellowish-orange needles, m.p. 156–157°; $E^{\text{mol}}_{1\,\text{cm.}}$ 6.78 × 10⁴ at $\lambda_{\max}$ 388 mμ (in hexane).

*Anal.* Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 93.80; H, 6.17.

**3-*cis*-Biphenylenephenylhexatriene** ("*cis*-I").—A 50-mg. all-*trans* sample was melted and kept at 275–280° for 30

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(5) E. Barraclough, J. W. Batty, I. M. Heilbron and W. E. Jones, *J. Chem. Soc.*, 1549 (1939).

sec., then cooled rapidly and dissolved in the minimum amount of benzene. One volume of hexane was added and the solution developed on alumina–lime–Celite (45 × 4.5 cm.) with benzene:hexane (2:1):

| | |
|---|---|
| 243 | empty section |
| 135 | dark red (all-*trans*) |
| 8 | interzone |
| 53 | pale red (*cis*-I) |
| 11 | empty section |

A thin zone containing the *cis*-II and -III was washed into the filtrate. The *cis*-I zone was eluted with benzene + 5% alcohol and the solvents were removed to yield a yellow, powdery residue. The combined yields of *cis*-I obtained as described from 250 mg. of the *trans* form were dissolved in benzene and developed on magnesia–Celite (30 × 4.5 cm.) with benzene + 3% alcohol:

| | |
|---|---|
| 95 | empty section |
| 41 | dark red (all-*trans*, mostly formed *de novo*) |
| 14 | interzone |
| 63 | red (*cis*-I) |
| 87 | empty section |

The *cis*-I fraction was recrystallized from hot benzene by dropwise addition, with stirring, of methanol; yield 25 mg. of yellow needles, m.p. 165.5–167°; $E^{\mathrm{mol}}_{1\,\mathrm{cm.}}$ 5.67 × $10^4$ at $\lambda_{\max}$ 385.5 mμ (in hexane).

*Anal.* Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 94.10; H, 5.76.

**5-*cis*-Biphenylenephenylhexatriene** ("*cis*-II").—Three 100-mg. portions of the all-*trans* compound were melted, kept at 270–275° for 30 sec., then cooled rapidly, dissolved in benzene and developed with benzene + 8% acetone on magnesia–Celite (45 × 4.5 cm.):

| | |
|---|---|
| 31 | empty section |
| 120 | dark red (all-*trans* + some *cis*-I) |
| 113 | interzone |
| 48 | red (*cis*-II) |
| 6 | interzone |
| 31 | pale red (*cis*-III) |
| 101 | empty section |

After elution the *cis*-II isomer was rechromatographed on a similar column using benzene + 9% acetone as the developer; thus, some *trans* compound was eliminated; yield 8.3 mg. of pale yellow flat prisms, m.p. 122–123.5°; $E^{\mathrm{mol}}_{1\,\mathrm{cm.}}$ 5.25 × $10^4$ at $\lambda_{\max}$ 385 mμ (in hexane). For analysis the sample was recrystallized from ethanol.

*Anal.* Calcd. for $C_{24}H_{18}$: C, 94.09; H, 5.92. Found: C, 93.89; H, 6.06 (corrected for 0.35% ash).

TABLE III

RATIOS OF THE *trans* AND *cis* FORMS IN STEREOISOMERIC MIXTURES OF BIPHENYLENEPHENYLHEXATRIENE

| Steric form treated | Treatment | Ratio in recovered substance *trans*:*cis*-I:*cis*-II:*cis*-III | Loss (% of starting material) |
|---|---|---|---|
| *trans* | Iodine cat.[a] | 92:8:trace:trace | 18 |
| *trans* | Irradiation[b] | No effect | |
| *trans* | Insolation[c] | No effect | |
| *trans* | Refluxing[d] | No effect | |
| *trans* | Melting cryst.[e] | 78.5:16.5:4:1 | 21 |
| *cis*-I | Iodine cat.[a] | 94:6:trace:trace | 23 |
| *cis*-I | Irradiation[b] | 2:98:0:0 | 1 |
| *cis*-I | Insolation[f] | 34:66:0:0 | 1 |
| *cis*-I | Refluxing[d] | No effect | |
| *cis*-II | Iodine cat.[a] | ~99:~1:0:0 | 26 |
| *cis*-II | Irradiation[g] | 3:0:97:0 | 1 |
| *cis*-II | Refluxing[d] | No effect | |
| *cis*-III | Iodine cat.[h] | 20:80:0:0 | 24 |
| *cis*-III | Irradiation[g] | ~0:~7:0:93 | 1 |
| *cis*-III | Refluxing[d] | No effect | |

[a] 2 min. at 60 cm. from light source (Pyrex flask). [b] 60 min. at 10 cm. from Photoflood bulb (Pyrex). [c] 120 min. in moderately intense sunlight (Pyrex). [d] Hexane solution refluxed for 30 min. in the dark. [e] 30 sec. at 320°. [f] 20 min. in intense sunlight (Pyrex). [g] 30 min. at 10 cm. from Photoflood bulb (Pyrex). [h] 30 min. at 200 cm. from light source (quartz cell); iodine 0.1% of substance.

**3,5-Di-*cis*-biphenylenephenylhexatriene** ("*cis*-III").—The *cis*-III fraction from the above column was combined with that obtained from 200 mg. of the all-*trans* form and developed with benzene + 9% acetone on magnesia–Celite (20 × 3.5 cm.):

| | |
|---|---|
| 11 | empty sections |
| 10 | red (all-*trans*) |
| 64 | interzone |
| 23 | pale red (*cis*-II) |
| 10 | interzone |
| 42 | red (*cis*-III) |
| 40 | empty section |

Yield 3.8 mg. of pale yellow crystals, m.p. 118.5–121°, $E^{\mathrm{mol}}_{1\,\mathrm{cm.}}$ 4.83 × $10^4$ at $\lambda_{\max}$ 379 mμ (in hexane).

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, CHEMICAL DIVISION, MERCK & CO., INC.]

# Synthesis of 8-Hydroxy-2-keto-5-methoxy-4a-methyl-2,3,4,4a,9,10-hexahydrophenanthrene

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8-Hydroxy-2-keto-5-methoxy-4a-methyl-2,3,4,4a,9,10-hexahydrophenanthrene has been prepared as a potential intermediate for the synthesis of 11-oxygenated steroids. The reactions used to convert 5-hydroxy-8-methoxytetralone-1 to 5-hydroxy-8-methoxy-1-methyltetralone-2 offer a general method for the synthesis of hydrophenanthrenes. The Robinson–Mannich base reaction to form the potential ring A has been broadened to include the use of aqueous reaction media.

This paper describes the synthesis of 8-hydroxy-2-keto-5-methoxy-4a-methyl-2,3,4,4a,9,10-hexahydrophenanthrene (XIX) and some related compounds. The method of synthesis was based in part on the previously described[2] preparation of 8-chloro-4a-ethyl-2-keto-5,6-dimethoxy-2,3,4,4a,9,10-hexahydrophenanthrene, a potential intermediate for the synthesis of morphine. Syntheses of the rather similar steroid intermediates, 8-hydroxy-2-keto-4a-methyl-2,3,4,4a,9,10-hexahydrophenanthrene[3] and 2-keto-5,8-dimethoxy-4a-methyl-2,3,4,4a,9,10-hexahydrophenanthrene[4] (XVIII) through somewhat different approaches have been

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(2) R. Ghosh and R. Robinson, *J. Chem. Soc.*, 506 (1944).

(3) J. W. Cornforth and R. Robinson, *ibid.*, 1855 (1949).

(4) C. A. Grob and W. Jundt, *Helv. Chim. Acta*, **31**, 1691 (1948).