

190. *Studies with Acetylenes. Part III.* The Synthesis of Three partly-cis-Diphenyloctatetraenes.*

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The two 1 : 8-diphenyloctatrienyne and a 1 : 8-diphenyloctadienediyne have been prepared and converted by partial hydrogenation into *cis*-1-, *cis*-3-, and *cis*-3 : *cis*-5-isomers of 1 : 8-diphenyloctatetraene.

DURING the fundamental studies by Zechmeister and his co-workers of the stereochemistry of polyenes¹ it was shown that irradiation of "all-*trans*" 1 : 8-diphenyloctatetraene gives three new geometrical isomers which were designated *cis*-I, *cis*-II, and *cis*-III.² These were assigned *cis*-3-, *cis*-1-, and either *cis*-1 : *cis*-3- or *cis*-1 : *cis*-5-structures,† respectively, from a consideration of their light-absorption properties and stabilities. In other investigations we prepared the two monoacetylenic analogues of 1 : 8-diphenyloctatetraene, which we have now used to test some of these stereochemical deductions. Few similar comparisons of synthetic materials and products of stereomutation have been reported previously.³

Copper-catalysed condensation⁴ of either the Grignard reagent or the lithium derivative of phenylacetylene with 1 : 4-dibromobut-*trans*-2-ene gave crystalline 1 : 8-diphenyloct-4-ene-1 : 7-diyne (I). On reduction this yielded the known 1 : 8-diphenyloctane,⁵ and with hot methanolic potassium hydroxide an isomeric hydrocarbon with

* Part II, Nigam and Weedon, *J.*, 1957, 3868.

† In this paper, when the position of a *cis*-structure is cited, it is to be understood that the other ethylenic centres are *trans*.

¹ Zechmeister, *Experientia*, 1954, **10**, 1; *Chem. Rev.*, 1944, **34**, 267.

² Zechmeister and Pinckard, *J. Amer. Chem. Soc.*, 1954, **76**, 4144; Lunde and Zechmeister, *Acta Chem. Scand.*, 1954, **8**, 1421; cf. Zechmeister and Le Rosen, *J. Amer. Chem. Soc.*, 1942, **64**, 2755.

³ Pinckard, Wille, and Zechmeister, *ibid.*, 1948, **70**, 1938; Robeson, Cawley, Weisler, Stern, Eddinger, and Chechak, *ibid.*, 1955, **77**, 4111; Oroshnik, *ibid.*, 1956, **78**, 2651; Gansser and Zechmeister, *Helv. Chim. Acta*, 1957, **40**, 1757.

⁴ Danehy, Killian, and Nieuwland, *J. Amer. Chem. Soc.*, 1936, **58**, 611.

⁵ Evans and Whalley, *J.*, 1954, 3642.

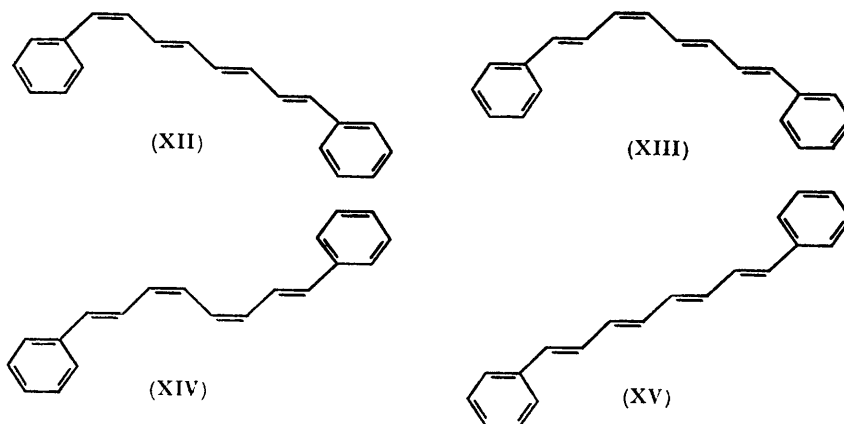
as the *cis*-1- (XII) and *cis*-3-isomers (XIII).^{*} Scale models indicate that a planar conformation of the *cis*-1-isomer is greatly strained owing to steric interference between the hydrogen atom at position 3 and one at an *ortho*-position in the aromatic ring, but that

TABLE I. Light absorption of diphenyloctatetraenes and their acetylenic analogues (λ_{max} in $\text{m}\mu$; $10^{-3}\epsilon$ in parentheses).

Acetylenes						
7-yne (II) ^a	—	—	—	365 (75)	385 (54)	
5-yne (X) ^a	—	—	—	365 (61)	386 (46.5)	
3 : 5-diyne (XI) ^a	—	—	335 (40)	360 (43.5)	380 (33)	
Tetraenes						
<i>cis</i> -1 (XII) ^b	268 *	280	—	368	—	
<i>cis</i> -II ^{b, d}	271	280	—	364	—	
<i>cis</i> -3 (XIII) ^c	275 (24.5)	284 (27.5)	355 (59.5)	373 (78)	393 (57)	
<i>cis</i> -I ^{b, d}	273 (23)	283 (28)	352 (57)	369 (78)	391 (56)	
<i>cis</i> -3 : <i>cis</i> -5 (XIV) ^c	—	—	350 (37)	370 (48)	390 (31)	
<i>cis</i> -III ^{b, d}	—	—	—	359	—	
" all- <i>trans</i> " (XV) ^a	—	—	355 (71.5)	373 (106)	395 (85)	
" all- <i>trans</i> " (XV) ^{b, d}	—	—	352 (74)	371 (108)	393 (85.5)	

* Inflection. ^a In CHCl_3 . ^b In hexane. ^c In cyclohexane. ^d Zechmeister and Pinckard.²

the *cis*-3 structure is subject to little strain. In agreement, the two *cis*-isomers have markedly different stabilities and light absorptions (Table I): the *cis*-1-form has a degraded spectrum lacking in fine structure, whereas the *cis*-3-isomer exhibits three intense light-absorption maxima at wavelengths almost identical with those of the " all-*trans* " form (XV), and a well-developed " *cis*-peak;" the *cis*-1-isomer was extremely labile to light and heat; both mono-*cis*-forms on irradiation were converted into mixtures from which



" all-*trans* " diphenyloctatetraene (XV) was isolated. These properties, and the infrared spectra of the *cis*-1- and *cis*-3-isomer, tally well with those reported by Zechmeister *et al.*² for their *cis*-II and *cis*-I isomers respectively, confirming their stereochemical conclusions.

A *cis*-3 : *cis*-5-structure was also considered by Zechmeister and Pinckard² for their *cis*-I isomer, but rejected in favour of the unhindered mono-*cis*-configuration. By oxidative coupling of styrylacetylene, and partial reduction of the resulting diacetylene (XI), the *cis*-3 : *cis*-5-isomer (XIV) has now been prepared. Its melting point is higher than that of the other known *cis*-isomers of 1 : 8-diphenyloctatetraene. Its main light-absorption maxima are similar to those of the *cis*-I isomer but are of lower intensity. Moreover, as predicted by Zechmeister and Pinckard, it shows no pronounced " *cis*-peak." On

* See footnote † on p. 933.

irradiation it yields a mixture from which "all-*trans*" diphenyloctatetraene has been isolated.

Some significant features of the infrared spectra of the diphenyloctatetraenes and their acetylenic analogues are summarised in Table 2. Both diphenylocta-*cis*-1- and

TABLE 2. *Infrared light absorption of diphenyloctatetraenes and their acetylenic analogues* (λ_{max} in μ with an indication of intensity; media shown in superscripts).

	CH in-plane deformation <i>cis</i> -CH:CH	CH out-of-plane deformation of <i>trans</i> -CH:CH	CH out-of-plane deformation <i>cis</i> -CH:CH	CH out-of-plane deformation of Ph groups
<i>Acetylenes</i>				
7-yne (II)	— ^f	10·07vs	— ^f	13·29s ^e 13·42s ^e
5-yne (X)	— ^f	10·21s ^f	10·53s ^f	— ^e 13·42vs ^e
3 : 5-diyne (XI)	— ^f	— ^f	10·51vs	— ^e 13·41vs ^e
<i>Tetraenes</i>				
<i>cis</i> -1 (XII)	7·08w ^a	10·00s ^a	10·27m ^a	? ? ?
<i>cis</i> -II ^h	7·05m ^f	10·05vs ^e	10·30s ^e	12·95s ^e — ^e 13·41s ^e
<i>cis</i> -3 (XIII)	7·05m ^e	10·11s ^e	10·31s ^e	12·89ms ^e — ^e 13·39s ^e
<i>cis</i> -I ^h	7·05m ^f	10·11s ^e	10·30s ^e	12·91ms ^e — ^e 13·37s ^e
<i>cis</i> -3 : <i>cis</i> -5 (XIV)	7·28m ^a	10·15ms ^a	10·55s ^a	12·85m ^e — ^e 13·54s ^e
<i>cis</i> -III ^h	7·00m ^f	10·10s ^e	10·30s ^e	12·95s ^e — 13·37s ^e
"all- <i>trans</i> " (XV)	— ^e	9·95s ^g	— ^g	— ^e 13·3** 13·45s ^e
"all- <i>trans</i> " (XV) ^h ...	— ^g	10·00s ^g	— ^g	— ^g 13·27s ^g — ^g
		9·90vs ^g	— ^f	— ^g 13·27s ^g — ^g

* Inflexion. ^a In CHCl₃. ^e In cyclohexane. ^f In KBr disc. ^g Mull in mineral oil.

^h Lunde and Zechmeister.² w, weak; m, medium; ms, medium strong; s, strong; vs, very strong.

cis-3-tetraene exhibit a band at 7·05—7·08 μ which is absent from the spectrum of the "all-*trans*" isomer, and can be attributed to the in-plane C—H bending vibration of the *cis*-double bonds: this band is absent from the spectra of the two diphenyloctatrienyne and the diphenyloctadienediyne. In the *cis*-3 : *cis*-5-isomer the band is displaced to 7·28 μ , and is thus similar to the 7·31 μ band previously observed with 1 : 4-diphenylbuta-*cis* : *cis*-diene.² If such a shift is tentatively assumed to be characteristic of two contiguous *cis*-double bonds, it indicates that Zechmeister's *cis*-III diphenyloctatetraene has the *cis*-1 : *cis*-5- rather than the *cis*-1 : *cis*-3-structure.

The band due to the C—H out-of-plane vibrations of *trans*-carbon-carbon double bonds is split in the *cis*-diphenyloctatetraenes. Lunde and Zechmeister² have suggested that the lower-wavelength maximum is associated with any conjugated *trans*-double bond, and the longer-wavelength band with a *trans*-double bond conjugated with a *cis*-double bond. The splitting is particularly pronounced in the *cis*-3 : *cis*-5-isomer. Both compounds, (X) and (XI), with a (*trans*-)double bond conjugated with an acetylenic, but not an ethylenic, linkage have a C—H deformation band at 10·5 μ . The marked differences in the 10·0—10·6 μ range, together with those in the 13·2—13·6 μ region associated with hydrogen out-of-plane rocking in the phenyl groups, enable the two diphenyloctatrienyne to be readily distinguished.

All the *cis*-diphenyloctatetraenes have a band at ca. 12·9 μ which is absent from the spectrum of the "all-*trans*" isomer, and may be attributed to C—H out-of-plane rocking in the *cis*-carbon-carbon double bonds. The absence of a band in this region in the spectra of the diphenyloctatrienyne and the diphenyloctadienediyne again shows that these compounds possess *trans*-configurations about their carbon-carbon double bonds.

EXPERIMENTAL

M. p.s were determined on a Kofler block and are corrected. Spectra reported in the Tables above are not repeated in this section.

All operations were carried out in an inert atmosphere. Those involved in the preparation

of the *cis*-diphenyloctatetraenes were performed, so far as possible, in the dark at temperatures not exceeding 20°.

1 : 8-Diphenyloct-4-ene-1 : 7-diyne (I).—(a) [With H. K. BLACK]. Cuprous chloride (0.6 g.) was added to a stirred and cooled (ice-salt) suspension of phenylacetylenylmagnesium bromide (prepared from 15.3 g. of phenylacetylene by the method of Black, Horn, and Weedon¹²) in ether (110 c.c.). 1 : 4-Dibromobut-*trans*-2-ene (16.1 g.) in ether (70 c.c.) was added during 40 min. The mixture was stirred at 20° overnight, then under reflux for 3 hr. and finally cooled. Excess of dilute acetic acid was added, and the ethereal layer was separated, washed with water, dried (Na₂SO₄), and evaporated. The residue (9.2 g.) solidified and had m. p. 58—61°. Recrystallisation from light petroleum (b. p. 40—60°) gave 1 : 8-diphenyloct-4-ene-1 : 7-diyne as long prisms, m. p. 60—61° (Found: C, 93.75, 93.4; H, 6.25, 6.3. C₂₀H₁₆ requires C, 93.7; H, 6.3%), λ_{max}. (in ethanol) 240 and 251 mμ (ε 37,000 and 38,500 respectively).

(b) Phenylacetylene (11.2 g.) in ether (16 c.c.) was added to a solution of phenyl-lithium (from 1.65 g. of lithium) in ether (80 c.c.), and the mixture was heated under reflux for 1½ hr. and then cooled. Cuprous chloride (0.4 g.) was added, followed by a solution of 1 : 4-dibromobut-*trans*-2-ene (10.7 g.) in ether (45 c.c.). The mixture was boiled under reflux for 24 hr., then cooled and poured into 10% v/v acetic acid (200 c.c.). Isolation and crystallisation of the product as in (a) gave the hydrocarbon (6.4 g., 54%), m. p. and mixed m. p. 59—61°.

1 : 8-Diphenyloctane.—A solution of the above diphenyloctenediyne (2.0 g.) in ethyl acetate (25 c.c.) was shaken with Adams catalyst (58 mg.) in hydrogen until absorption ceased (953 c.c. at 24°/758 mm., equivalent to 5.0 double bonds). Removal of catalyst and solvent, and distillation of the residue, gave 1 : 8-diphenyloctane (1.4 g.), b. p. 137—138°/0.1 mm., n_D²¹ 1.5313. Its infrared absorption was in good agreement with that reported by Evans and Whalley⁵ who give b. p. 138—142°/0.1—0.2 mm., n_D²³ 1.5290.

5-Phenylpent-1-en-4-yn-3-ol (III).—Acraldehyde (16.0 g.) in ether (100 c.c.) was added during 30 min. to a stirred suspension of phenylacetylenylmagnesium bromide (prepared from 26 g. of phenylacetylene) in ether (200 c.c.). The mixture was stirred at 20° for 2 hr. and for 30 min. under reflux. It was then cooled, and an excess of saturated aqueous ammonium chloride was added. Isolation of the product with ether, and distillation, gave the *alcohol* (21.0 g.), b. p. 100—104°/1 mm., n_D²³ 1.5740—1.5747, n_D³¹ 1.5710—1.5720 (Found: C, 83.45; H, 6.5. C₁₁H₁₀O requires C, 83.55; H, 6.35%).

1-Bromo-5-phenylpent-2-en-4-yne (IV).—Phosphorus tribromide (10.0 g.) in ether (10 c.c.) was added during 30 min. to a stirred and cooled (−8°) solution of the preceding alcohol (19.0 g.) in ether (50 c.c.). The mixture was stirred at 0° for 1 hr., then at 20° for 3 hr. The resulting product was poured on ice and water. Isolation with ether and distillation gave the *bromide* (21.0 g.), b. p. 96—100°/1 mm., n_D²² 1.6450—1.6465 (Found: C, 59.9; H, 4.4. C₁₁H₉Br requires C, 59.7; H, 4.05%), λ_{max}. (in ethanol) 285 mμ (ε 22,000). For the corresponding alcohol Haynes *et al.*¹³ report maxima at 259, 272, and 289 mμ (ε 19,000, 26,000 and 21,000 respectively).

Triphenyl-(5-phenylpent-2-en-4-ynyl)phosphonium Bromide (V).—The preceding bromide (6.0 g.) was added to a shaken and cooled (−10°) solution of triphenylphosphine (7.4 g.) in benzene (18 c.c.). The mixture was kept at 20° for 48 hr., and the solid (13 g.) which had separated was then collected. Two crystallisations from alcohol gave the *phosphonium bromide* as colourless plates, m. p. 192—193° (Found: C, 71.2, 71.15; H, 5.45, 5.6. C₂₆H₂₄BrP, ½EtOH requires C, 71.15; H, 5.35%), λ_{max}. (in ethanol) 268 and 298 mμ (ε 33,500 and 21,000 respectively).

1 : 8-Diphenylocta-1 : 3 : 5-trien-7-yne (II).—(a) 1 : 8-Diphenyloct-4-ene-1 : 7-diyne (1.0 g.) was added to a solution of potassium hydroxide (4.0 g.) in methanol (40 c.c.), and the mixture was stirred at 80° for 3 hr. The resulting orange solution was decanted from an insoluble gum and cooled. The crystals which separated (103 mg., 10%) were collected and had m. p. 137—145°. Recrystallisation from *n*-hexane gave 1 : 8-diphenylocta-1 : 3 : 5-trien-7-yne as yellow plates, m. p. 146—147° (Found: C, 93.6; H, 6.55. C₂₀H₁₆ requires C, 93.7; H, 6.3%).

In a small-scale experiment under identical conditions spectral examination of the reaction mixture indicated 54% conversion of the diphenyloctenediyne into fully conjugated isomers.

(b) Butyl-lithium (equiv. to 56 mg. of lithium) in ether (8.5 c.c.) was added to a suspension of the triphenyl(phenylpentenylyl)phosphonium bromide (2.7 g.) in ether (30 c.c.), and the

¹² Black, Horn, and Weedon, *J.*, 1954, 1704.

¹³ Haynes, Heilbron, Jones, and Sondheimer, *J.*, 1947, 1583.

mixture was stirred for 1½ hr. at 20°. Cinnamaldehyde (1.1 g.) was then added, and the mixture stirred at 20° for 20 min., then under reflux for 20 min. The mixture was cooled and dilute hydrochloric acid was added. The mixture was filtered and the solid was extracted with ether. The ethereal filtrate and washings were combined, washed with aqueous sodium carbonate, dried (Na₂SO₄), and evaporated. Crystallisation of the residue (1.0 g.) from aqueous alcohol gave yellow needles (150 mg.), m. p. 140—146°. Recrystallisation from the same solvent gave the hydrocarbon, m. p. 146—147.5° undepressed on admixture with a specimen from (a). The two samples had the same spectra. Admixture with a specimen of 1 : 8-diphenylocta-1 : 3 : 7-trien-5-yne gave a depression of 2°.

1 : 8-Diphenylocta-cis-1 : trans-3 : trans-5 : trans-7-tetraene (XII).—A solution of the preceding diphenyloctatrienyne (50 mg.) in ethyl acetate (10 c.c.) containing quinoline (20 mg.) was shaken in the dark with Lindlar catalyst¹⁰ (50 mg.) in hydrogen until 1.1 mol. had been absorbed (4.81 c.c. at N.T.P.). The catalyst was filtered off and the solvent was evaporated under reduced pressure. The residue was triturated with a small volume of methanol, and the solid was separated by centrifugation and removal of the supernatant liquid with a pipette. Two further washings with methanol in the same way gave the crude mono-cis-tetraene (ca. 21 mg.) which was dissolved in hexane and examined spectrally [max. at 280 and 368 mμ and an inflexion at 268 mμ (*E* 0.109, 0.807, and 0.101 respectively) (Zechmeister and Pinckard report maxima at 271 and 364 mμ and an inflexion at 280 mμ)]. After exposure to light for 2 days the hexane solution exhibited maxima at 262, 353, 371, and 393 mμ (*E* 0.062, 0.815, 1.151, and 1.01 respectively).

The preceding partial hydrogenation was repeated and, after removal of the catalyst, the ethyl acetate solution was kept in sunlight for 24 hr. Evaporation of the solvent, trituration of the residue at 0° with methanol, and filtration then gave a mixture (25 mg.) of geometrical isomers of diphenyloctatetraene. Crystallisation from chloroform gave the "all-trans" isomer (9 mg.), m. p. 235—236°, undepressed on admixture with a specimen prepared according to Kuhn and Winterstein's method.¹⁴

1 : 6-Diphenylhexa-1 : 3-dien-5-yne.—Phenyl-lithium (from 108 mg. of lithium) in ether (30 c.c.) was added to a suspension of the triphenyl(phenylpentenylyl)phosphonium bromide (2.9 g.) in ether (10 c.c.), and the mixture was stirred for 3 hr. Benzaldehyde (1.3 g.) was added and the mixture was stirred at 20° for 2½ hr. and under reflux for 10 min. The mixture was cooled and a solution of concentrated hydrochloric acid (3 c.c.) in water (50 c.c.) was added. Isolation of the crude product (1.0 g.) in the usual way, and crystallisation from aqueous alcohol, gave yellow needles (170 mg.), m. p. 99—100°. Recrystallisation from the same solvent gave the hydrocarbon, m. p. 103—104° (Found: C, 93.6, 93.55; H, 6.55, 6.45. C₁₈H₁₄ requires C, 93.9; H, 6.1%), λ_{max.} (in chloroform) 265 and 340 mμ (ε 4800 and 31,000 respectively).

4-Chloro-4-phenylbut-1-yne (VII; X = Cl).—Reaction of 1-phenylbut-3-yn-1-ol¹⁵ (10.0 g.) in pyridine (5.6 g.) with thionyl chloride (8.0 g.) by the method of René-Golse and Le van Thoi⁸ gave the chloride (5.5 g.) as a pale yellow mobile liquid, b. p. 72—84°/1 mm., n_D²³ 1.5549—1.5560 (lit.,⁸ b. p. 75°/2 mm., n_D²⁰ 1.5555).

4-Bromo-4-phenylbut-1-yne (VII; X = Br).—Phosphorus tribromide (11.5 g., 15% excess) was added during 20 min. to a cooled (ice) and stirred solution of 1-phenylbut-3-yn-1-ol (15 g.) and pyridine (4 c.c.) in ether (25 c.c.). The mixture was stirred for a further 15 min. at 0° and for 20 min. at 35—40°. A colourless solid which had separated was filtered off and extracted with ether (200 c.c.). The filtrate and extracts were combined, washed with water, saturated sodium carbonate, and again with water, then dried (Na₂SO₄) and evaporated. Distillation of the residue gave the bromide (12 g., 57%) as a pale yellow liquid, b. p. 88—89°/0.5 mm., n_D²¹ 1.5850, which solidified at 0° and after crystallisation from ethanol had m. p. 31° (lit.,⁸ b. p. 95°/2 mm., n_D²⁰ 1.5747), and λ_{max.} (in alcohol) 223 mμ (ε 6300).

3 : 4-Dibromo-1-phenylbut-1-ene (VIII).—1-Phenylbuta-1 : 4-diene¹⁶ was treated with bromine according to Riiber's directions.⁹ The dibromide had m. p. 94—95° (Riiber⁹ gives m. p. 94°).

1-Phenylbut-1-en-3-yne (Styrylacetylene) (IX).—(a) Dehydrochlorination of 4-chloro-4-phenylbut-1-yne (5.7 g.) with potassium hydroxide (5.0 g.) in ethanol (40 c.c.) by the method of René-Golse and Le van Thoi⁸ gave 1-phenylbut-1-en-3-yne as a very unstable liquid, b. p.

¹⁴ Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 87.

¹⁵ Henbest, Jones, and Walls, *J.*, 1949, 2696.

¹⁶ Braude, Jones, and Stern, *J.*, 1947, 1087.

56—60°/5 mm., n_D^{21} 1.6068 (lit.,⁸ b. p. 59°/2 mm., n_D^{20} 1.6123). The yields in successive experiments were 30, 50, and 40%. The product readily gave a copper salt with ammoniacal cuprous chloride.

(b) 4-Chloro-4-phenylbut-1-yne (7.8) was added in 5 min. to a stirred solution of sodamide (prepared¹⁷ from 3.5 g. of sodium) in liquid ammonia (150 c.c.), and the mixture was stirred for 4 hr. Ammonium chloride (12 g.) was added cautiously, and the ammonia was allowed to evaporate overnight. Water (200 c.c.) was added to the residue, and the product was extracted with ether (150 c.c.). The extract was washed with water, dried (Na_2SO_4), and evaporated. Distillation of the residue gave the hydrocarbon (3.0 g., 55%), b. p. 56°/1 mm., n_D^{24} 1.6095.

(c) Treatment of 4-bromo-4-phenylbut-1-yne (11.8 g.) with sodamide (from 3.5 g. of sodium) in liquid ammonia (200 c.c.), and isolation of the product in the same way, gave the hydrocarbon (5.7 g., 80%), b. p. 46°/5 mm., n_D^{22} 1.6120, λ_{max} (in ethanol) 220, 227, and 278 μ (ϵ 15,500, 11,000, and 30,500 respectively). The mercury salt crystallised from benzene and had m. p. 163°.

(d) A solution of 3 : 4-dibromo-1-phenylbut-1-ene (32 g.) in ether (150 c.c.) was added slowly to a solution of sodamide (from 8.0 g. of sodium) in liquid ammonia (400 c.c.), and the mixture was stirred for 3 hr. Addition of ammonium chloride (20 g.), and isolation of the product as described under (b), gave the hydrocarbon (4.4 g., 30%), b. p. 58—59°/2 mm., n_D^{21} 1.6157.

Copper Styrylacetylide.—Cuprous chloride (8.0 g.) was added to freshly prepared, saturated aqueous ammonium carbonate (400 c.c.). To the resulting suspension dilute aqueous ammonia was added cautiously until a clear blue solution was obtained. To this was added 1-phenylbut-1-en-3-yne (3.0 g.) in ethanol (25 c.c.), and the mixture was stirred vigorously for 30 min. The yellow precipitate was collected, washed successively with dilute ammonia, water, ethanol, and ether, and dried in a vacuum-desiccator, to give the copper acetylide (3.9 g.) as an orange powder.

The different batches of 1-phenylbut-1-en-3-yne reported above all gave the copper acetylide in 80—90% yield.

1 : 8-Diphenylocta-1 : 3 : 7-trien-5-yne (X).—Finely divided copper styrylacetylide (1.5 g.) was added to acetic acid (60 c.c.) in a 250 c.c. two-necked flask fitted with an efficient reflux condenser. The mixture was boiled and, when the suspended copper salt had been converted into a flocculent brown precipitate (5—10 min.), air was aspirated through the mixture at a rate which was just sufficient to cause appreciable loss of solvent through the condenser. After the mixture had developed a greenish colour (40—50 min.), a few drops were withdrawn every 2 min., diluted with water, and extracted with ether. When no insoluble copper salt was visible at the water-ether interface in the test sample, the reaction was interrupted, and the deep green mixture was cooled, diluted with water (2 vol.), and extracted with ether. The extracts were washed with aqueous sodium carbonate until free from acetic acid, then with water, dried (Na_2SO_4), and evaporated. Repeated recrystallisation of the residue (0.4 g., 40%), m. p. 135—147°, from ethanol gave 1 : 8-diphenylocta-1 : 3 : 7-trien-5-yne (0.2 g.) as pale yellow plates, m. p. 146—147° (Found: C, 93.55; H, 6.4. $\text{C}_{20}\text{H}_{16}$ requires C, 93.7; H, 6.3%).

Continuation of the aeration after the stage indicated above resulted in a very impure product.

1 : 8-Diphenylocta-trans-1 : cis-3 : trans-5 : trans-7-tetraene (XIII).—A solution of the preceding diphenyloctatrienyne (53.0 mg.) in ethyl acetate (5 c.c.) was shaken with Lindlar catalyst¹⁰ (50 mg.) in the dark in an atmosphere of hydrogen. After 4 hr., when 1.1 mol. of hydrogen had been absorbed (5.23 c.c. at N.T.P.), the reaction was interrupted and the catalyst and solvent were removed. Crystallisation of the residue from ether-light petroleum (b. p. 40—60°) gave the mono-cis-tetraene (32 mg.) as yellow needles, m. p. 135—136° (Found: C, 93.15; H, 7.05. Calc. for $\text{C}_{20}\text{H}_{18}$: C, 92.95; H, 7.05%). The same m. p. was observed when determined in an evacuated capillary tube (Zechmeister and Pinckard² give m. p. 139—141°).

When the molten tetraene was heated at 160—170° it resolidified and afterwards remelted at 227—230°.

Irradiation of a solution of the mono-cis-tetraene (1.6 mg.) and a trace of iodine (0.027 mg.) in cyclohexane (50 c.c.) with a "photoflood" lamp for 15 min. gave a mixture of stereoisomers, λ_{max} 275, 285, 355, 375, and 395 μ (ϵ 6000, 6000, 69,000, 98,000, and 77,000).

A solution of the mono-cis-tetraene (10 mg.) in benzene (15 c.c.) and hexane (50 c.c.) was kept before an ultraviolet lamp for 15 min. and then evaporated. Crystallisation of the residue from chloroform gave "all-trans" 1 : 8-diphenyloctatetraene (4 mg.), m. p. and mixed m. p. 232—234°.

¹⁷ Vaughn, Vogt, and Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2120.

1 : 8-Diphenylocta-1 : 7-diene-3 : 5-diyne (XI).—(a) Finely divided copper styrylacetylde (2.0 g.) was added to a solution of potassium ferricyanide (8.0 g.) in water (70 c.c.), and the suspension was stirred vigorously for 3 hr. at 60—80°. The resulting thick brown suspension was extracted repeatedly with ether. The extracts were combined, washed with water, dried (Na_2SO_4), and evaporated. Crystallisation of the residue from chloroform–light petroleum (b. p. 40—60°) gave the *diphenyloctadienediyne* (0.17 g.) as pale yellow needles, m. p. 133—134° (Found: C, 94.25; H, 5.8. $\text{C}_{20}\text{H}_{14}$ requires C, 94.5; H, 5.5%).

(b) Finely divided copper styrylacetylde (1.3 g.) was added to a solution of ammonium chloride (12.0 g.) and cuprous chloride (8.0 g.) in water (50 c.c.) and 9*N*-hydrochloric acid (1 c.c.). The suspension was shaken in oxygen for 6 hr. during which 800 c.c. of oxygen were absorbed. Dilute hydrochloric acid was added to decompose a greenish complex which had separated, and a yellow precipitate was then filtered off. By extraction with ether the yellow solid was separated into an insoluble residue of unchanged copper styrylacetylde (0.3 g.) and the required hydrocarbon (0.2 g.), m. p. and mixed m. p. 133—134°.

(c) Freshly prepared 1-phenylbut-1-en-3-yne (2.0 g.) in alcohol (30 c.c.) was added to a solution of cuprous ammonium chloride (from 16.2 g. of ammonium chloride and 10.3 g. of cuprous chloride) in water (200 c.c.) which had been acidified to pH 4—5 by the addition of concentrated hydrochloric acid (3 drops). The mixture was shaken in oxygen until absorption ceased (600 c.c.; 6 hr.). Dilute hydrochloric acid was added to dissolve a light green precipitate, which had formed during the reaction, and a yellow solid was filtered off, dried, and extracted with ether. Evaporation of the extract and crystallisation of the residue from chloroform–light petroleum (b. p. 40—60°) yielded the required hydrocarbon (1.25 g., 60%), m. p. and mixed m. p. 133—133.5°.

1 : 8-Diphenylocta-trans-1 : cis-3 : cis-5 : trans-7-tetraene (XIV).—A solution of the preceding diphenyloctadienediyne (52.2 mg.) in ethyl acetate (5 c.c.) was shaken with Lindlar catalyst (50 mg.) in the dark in an atmosphere of hydrogen until 2.1 mol. of gas had been absorbed (8—12 hr. in different experiments). Removal of catalyst and solvent at 20° and crystallisation of the residue at –40° in the dark from ether–light petroleum gave the *di-cis-tetraene* (16 mg.) as yellow plates, m. p. 191—193° (Found: C, 92.5; H, 6.95. $\text{C}_{20}\text{H}_{18}$ requires C, 92.95; H, 7.05%).

When the molten tetraene was heated it resolidified and afterwards remelted at 222—226°.

Irradiation of a solution of the *di-cis-tetraene* (1.6 mg.) and a trace of iodine (0.027 mg.) in cyclohexane (50 c.c.) with an ultraviolet lamp for 15 min. gave a mixture of stereoisomers, λ_{max} 275, 285, 355, 375, and 395 m μ (ϵ 6500, 6500, 65,000, 98,000, and 79,000 respectively).

A solution of the *di-cis-tetraene* (7 mg.) in benzene (15 c.c.) and hexane (50 c.c.) was kept before an ultraviolet lamp for 15 min. and then evaporated. Crystallisation of the residue from chloroform gave "all-*trans*" 1 : 8-diphenyloctatetraene (4 mg.), m. p. and mixed m. p. 234—235.5°.

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