"Bistetracyclones" and "Bishexaphenylbenzenes"

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Four representatives of a new class of colored compounds, the bistetraphenylcyclopentadienones (compound 1), have been prepared, linked by a direct bond, $-CH_2-$, O, and S, respectively. New intermediates for their syntheses have been described including the required bisdeoxybenzoins and bisbenzils. The absorption spectra of the bistetracyclones have been briefly discussed. Analogs of hexaphenylbenzene, prepared from each by reaction with tolan, produced a unique group of compounds melting in the range 440–460°.

Previous papers[3] have discussed the syntheses and electronic spectra of tetracyclone and its derivatives. In the present paper we wish to report on the syntheses and electronic spectra of four bistetracyclones **1**.

Syntheses.—The most generally useful synthesis for tetracyclone employs the base-catalyzed condensation of benzil and benzyl ketone.[4] In choosing a route to the bistetracyclones we selected the condensation of two moles of benzyl ketone with an appropriate bisbenzil rather than its obvious alternative, because the bisbenzils appeared to be more readily available synthetically. Chart I outlines the paths selected.

Diphenylmethane, diphenyl ether, and diphenyl sulfide reacted with two moles of phenylacetyl chloride to give the bisdeoxybenzoins **2b,c,d** without exceptional difficulty. However, diphenyl failed to give a bisphenylacetyl derivative. The alternative path required 4,4′-dicyanobiphenyl which had already been described.[5] Using a ratio of from 4 to 5 moles of benzylmagnesium chloride per nitrile group, followed by acid hydrolysis, gave the bisdeoxybenzoin **2a** in 63% yield.

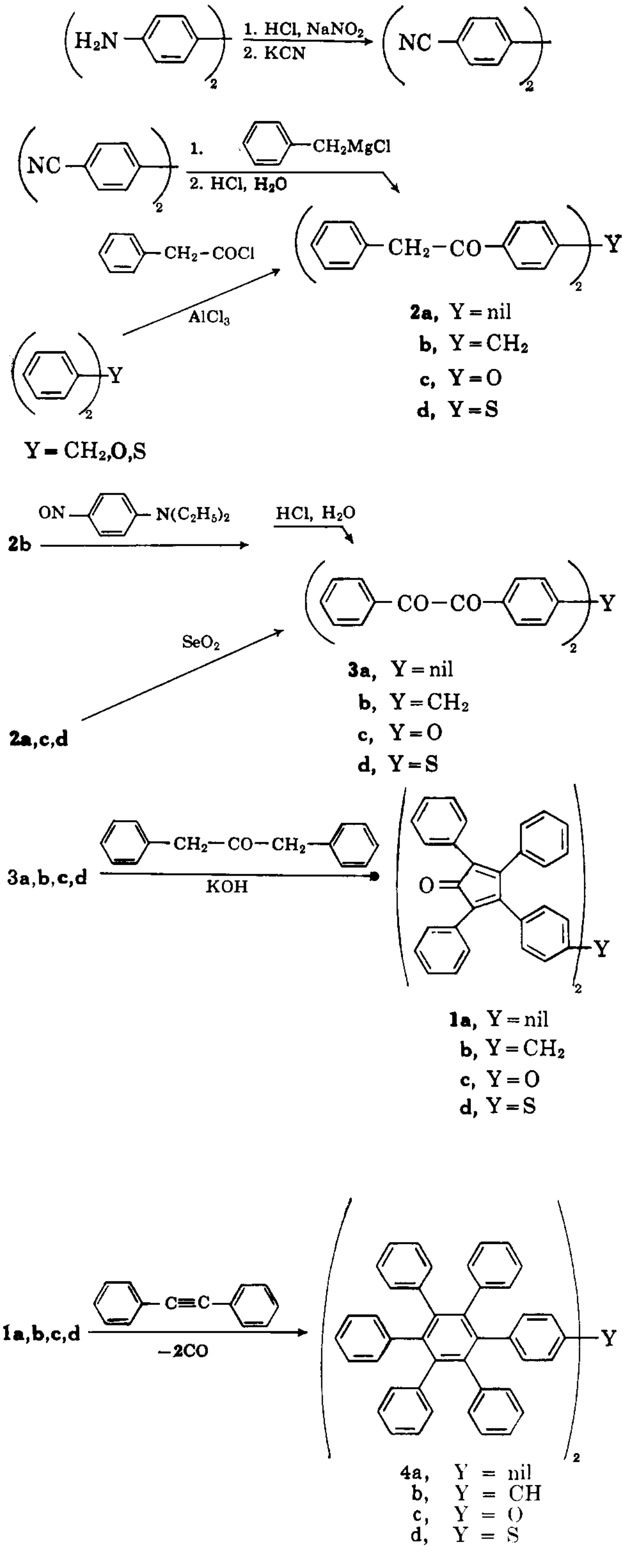
Conversion of compounds **2a,c,d** to the bisbenzils **3a,c,d** was effected by means of selenium dioxide in 53–80% yields.

In the case of **2b** the conversion was effected *via* condensation with *p*-nitrosodiethylaniline followed by acid hydrolysis in 69–76% yield.

Condensation of compounds **3** with benzyl ketone proceeded without particular difficulty to give the bistetracyclones **1**, provided the ratio of benzyl ketone to bisbenzil was about 2 : 1.

For derivative purposes the bistetracyclones were converted to the hexaphenylbenzene analogs by reaction with diphenylacetylene, just as tetracyclone itself is converted to hexaphenylbenzene. Since tetracyclone, m.p. 220°, gives hexaphenylbenzene, m.p. 421–422°,[6] it was anticipated that the bis compounds **4** would have unusually high melting points. The observed melting points were indeed quite high, ranging from **4a**, m.p. 440–442°, to **4c**, m.p. 456–459°. The melting point of **4a** may be compared with that of octaphenylquinquephenyl (I), m.p. 462–463° (uncor.),[7] and of linear sexiphenyl (II), m.p. 475°.[8]

CHART I



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(1) (a) From the B.S. thesis (1960) and part of the Ph.D. research at the Polytechnic Institute of Brooklyn; (b) from the B.S. thesis, Polytechnic Institute of Brooklyn, 1961; (c) Undergraduate Research Participant for the Summer, 1960, NSF G12636.

(2) To whom inquiries should be sent.

(3) See V. F. D'Agostino, M. J. Dunn, A. E. Ehrlich, and E. I. Becker, *J. Org. Chem.*, **23**, 1539 (1956), and papers cited therein.

(4) O. Grummitt and J. R. Johnson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 806.

(5) T. S. Work, *J. Chem. Soc.*, 1315 (1940).

(6) W. Dilthey, W. Schommer, and O. Trösken, *Ber.*, **66**, 1627 (1933).

(7) W. Ried and K. H. Bönninghausen, *Chem. Ber.*, **93**, 1769 (1960).

(8) R. Pummer and K. Bittner, *ibid.*, **57**, 87 (1924).

TABLE I

PHYSICAL CONSTANTS AND ANALYSES FOR INTERMEDIATES AND BISCYCLONES

Compound no.	Y	M.p., °C.	Yield, %	Formula	Carbon		Hydrogen		Sulfur	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
2a	Nil	225.5–226.5[a]	63	$C_{28}H_{22}O_2$						
2b	CH_2	144.0–145.0	48	$C_{29}H_{24}O_2$	86.11	86.26	5.98	6.34		
2c	O	169.0–170.0	77	$C_{28}H_{22}O_3$	82.74	82.61	5.46	5.44[b]		
2d	S	198.5–199.5[c]	48	$C_{28}H_{22}O_2S$	79.60	79.84	5.25	5.38	7.57	7.34
3a	Nil	203.0–204.0	60	$C_{28}H_{18}O_4$	80.37	80.48	4.34	4.51		
3b	CH_2	144.0–144.5	76	$C_{29}H_{20}O_4$	80.54	80.49	4.66	4.82		
3c	O	106.4–107.4	81	$C_{28}H_{18}O_5$	77.41	77.20	4.18	4.15[d]		
3d	S	90.0–91.6	53	$C_{28}H_{18}O_4S$	74.65	75.18	4.03	4.45	7.11	6.92
1a	Nil	293.8–294.5	89	$C_{58}H_{38}O_2$	90.83	91.29	4.99	5.24		
1b	CH_2	248.2–249.7	40	$C_{59}H_{40}O_2$	90.74	90.36	5.16	5.21		
1c	O	256.0–258.0	79	$C_{58}H_{38}O_3$	88.98	88.71	4.89	4.89		
1d	S	277.0–279.0	53	$C_{58}H_{38}O_2S$	87.18	87.32	4.79	4.73	4.01	4.31
4a	Nil	440.0–442.0[e]	81	$C_{84}H_{58}$	94.52	94.57	5.48	5.61		
4b	CH_2	440.0–444.0[e]	86	$C_{85}H_{60}$	94.41	94.31	5.59	5.57		
4c	O	456.0–459.0[e]	61	$C_{84}H_{58}O$	93.13	93.23	5.40	5.52		
4d	S	442.0–446.0[e]	36	$C_{84}H_{58}S$	91.77	91.48	5.32	5.42	2.91	2.91

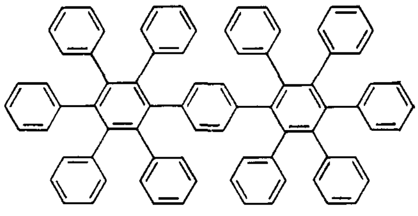
[a] Lit.[11] m.p. 224° (uncor.). [b] Mol. wt. (Rast camphor): calcd., 406; found, 411. [c] Lit.[12] m.p. 194–195°. [d] Mol. wt. (Rast camphor): calcd., 434; found, 436. [e] Melting points taken on an electrically heated aluminum block.

TABLE II

SPECTRAL CHARACTERISTICS OF BISCYCLONES

Compound, no.	Y	Solvent	λ_1[a] (ϵ_{m_1})[b]	λ_2 (ϵ_{m_2})[b]	λ_3 (ϵ_{m_3})[b]	λ_4 (ϵ_{m_4})[b]	λ_5 (ϵ_{m_5})[b]
1a	Nil	C[c]	255 (30.4)	297 (18.60)	368 (15.50)		
		B[d]				463 (2.1)	504 (2.1)
1b	CH_2	C	261 (55.5)	......	347 (16.96)		
		B				463[e] (2.2)	502 (2.2)
1c	O	C	260 (46.8)	274[f] (39.2)	368 (15.82)		
		B				463[e] (1.2)	507 (1.8)
1d	S	C	257 (31.2)	276[f] (22.7)	375 (9.38)		
		B				463 (2.2)	502 (2.3)

[a] Millimicrons. [b] All ϵ_m values are 10^{-3}. [c] Cyclohexane. [d] Benzene. [e] Shoulder. [f] Inflection.



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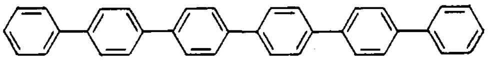

II

Finally, all of the products **4** are colorless as is also true for hexaphenylbenzene.

Spectra.—The electronic spectra of the biscyclones are shown in Fig. 1 and 2 in cyclohexane and benzene, respectively. For compounds **1b, 1c,** and **1d,** the spectra are largely similar to that for tetracyclone. The broad absorption band of low intensity near 500 mμ corresponds to that for tetracyclone at 512 mμ. A band at 347–375 mμ also appears which corresponds to that for tetracyclone at 343 mμ (benzene). The bathochromic shift of this band compared to that of tetracyclone and the concomitant hypsochromic shift of the 512-mμ band are in accord with the observations for aryloxy and arylthio cyclones observed previously; namely, that the aryloxy and arylthio groups are electronic releasing and increase the intensity of the excited state associated with the electronic path containing it,[3] and thus increasing the oscillator strength of the other.[9]

A new band is clearly observed for **1a.** The intensity of the band diminishes in intensity in going to **1d,** to **1c,** and to **1b.** Proof of the origin of this band is not yet available, but a tentative hypothesis is that for **1a** there is a new type of excitation possible involving both tetracyclone moieties simultaneously, and that, in **1b–1d,** this kind of excitation is falling off as the atom Y can less and less serve as a transmitter of electronic effects between the cyclone moieties. In any case a new series of biscyclones is being prepared with increasing numbers of carbon atoms between the cyclone moieties.

Experimental

4,4'-Dicyanobiphenyl.—This method of preparation was adapted from that of T. S. Work.[5] Sixty-five grams (0.25 mole) of benzidine dihydrochloride was dissolved in 100 ml. of concentrated hydrochloric acid and 400 g. of ice added. Sodium nitrite (about 110 ml. of 30% solution) was added slowly until the nitrous acid just failed to be consumed. The solution was then neutralized with saturated aqueous sodium carbonate and then added slowly with stirring to a solution of cuprous cyanide complex [from 45.0 g. (0.5 mole) of cuprous cyanide and 65.0 g. (1.0 mole) of potassium cyanide in 1060 ml. of water] at 90°.

After cooling to room temperature, the light yellow-brown solid was filtered and dried in an oven at 100° for 12 hr., affording 110.5 g. of product, which was then extracted in a Soxhlet extractor with 600 ml. of chloroform until the chloroform solution came

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(9) E. L. Shapiro and E. I. Becker, *J. Am. Chem. Soc.*, **75**, 4769 (1953).

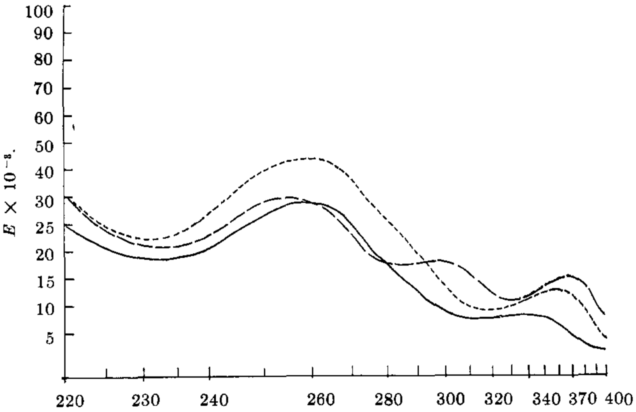

Fig. 1.—Ultraviolet absorption spectra of tetracyclone and biscyclones in cyclohexane; ——— tetracyclone, ------ bis-oxygen-cyclone (1c), — — bis-nil-cyclone (1a).

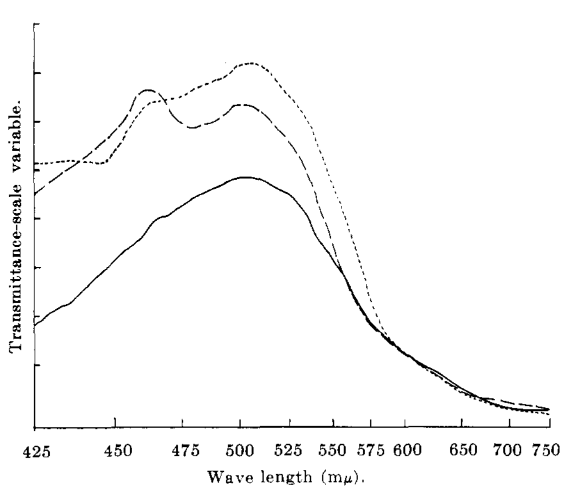

Fig. 2.—Visible transmittance spectra of tetracyclone and biscyclones and benzene; ——— tetracyclone, ------ bis-oxygen-cyclone (1c), — — bis-nil-cyclone (1a).

over clear. Distillation of the chloroform gave 50.0 g. of a light yellow-brown material. Sublimation of this product at 150° (20 mm.) gave 24.5 g. (0.12 mole, 48.0%) of colorless 4,4'-dicyanobiphenyl, m.p. 237-238° [lit.[10] m.p. 234°, lit.[11] 235° (uncor.)].

4,4'-Diphenacetylbiphenyl (2a).—To a stirred solution of benzylmagnesium chloride [from 2.4 g. (0.10 g.-atom) of magnesium, 10.1 g. (10.0 ml., 0.080 mole) of benzyl chloride, and 160 ml. of ether] was added dropwise a solution of 2.04 g. (10 mmoles) of 4,4'-dicyanobiphenyl in 100 ml. of tetrahydrofuran. After heating the mixture for 1 hr. and then stirring for 24 hr., 200 ml. of benzene was added, and the tetrahydrofuran and ether were distilled. The benzene solution was poured slowly onto a mixture of 500 g. of ice and 300 ml. of concentrated hydrochloric acid, and then the entire mixture was returned to the flask and refluxed for 24 hr. At this time the benzene layer was deep yellow-green in color. After cooling the entire mixture in ice, the crude solid (3.2 g.) was filtered and air-dried, m.p. 226-230°. Concentration of the benzene layer afforded no more solid.

Recrystallization from 250 ml. of methylene chloride (0.5 g. of charcoal) afforded 2.45 g. (6.3 mmoles, 62.7%) of yellowish white material, m.p. 225.5-226.5° [lit.[11] m.p. 224° (uncor.)].

***p,p'*-Diphenacetyldiphenylmethane (2b).**—To a stirred mixture of 32 g. (0.24 mole) of anhydrous aluminum chloride and 100 ml. of carbon disulfide cooled by means of an ice bath, there was added a mixture of 16.8 g. (16.0 ml., 0.10 mole) of diphenylmethane and 37.1 g. (32.0 ml., 0.24 mole) of phenylacetyl chloride for 1 hr. The reaction mixture was allowed to stand for one additional hour at room temperature and was then refluxed for 1.5 hr. or until all the hydrogen chloride has ceased to evolve. After cooling and pouring the contents onto a mixture of 100 g. of ice and 50 g. of hydrochloric acid, a yellow-white precipitate separated. The carbon disulfide was distilled with steam (caution!) and the resulting solid was taken up in 300 ml. of benzene. Concentration to 50 ml. afforded 45.5 g. of impure yellow-orange solid. Recrystallization from benzene gave 26.0 g. of impure, orange solid. Chromatography from 200 ml. of methylene chloride on Woelm acid alumina using methylene chloride as eluent, gave a colorless band which was collected in the eluate. Concentration to 50 ml., addition of 25 ml. of benzene, and cooling afforded 11.5 g. (0.028 mole, 28%) of white solid, m.p. 144-145°. Continued elution with pure chloroform afforded 10 g. of light orange solid, m.p. 117-120°. Subjecting this fraction to chromatography from methylene chloride as described previously produced 8.0 g. of pure product for an over-all yield of 19.5 g. (0.0482 mole, 48.2%), m.p. 144.0-145.0°.

***p*-Phenacetylphenyl Sulfide (2d).**—The conditions and ratio of reactants for this acylation are those given in the preceding paragraph, but the work-up was different. The carbon disulfide was distilled from the mixture and the solid which remained was filtered and dissolved in 400 ml. of hot chlorobenzene (0.1 g. of carbon). Filtering the cooled solution, slurrying the collected crystals with pentane, filtering again, and drying, gave 41.2 g. of crude product. Recrystallization from pyridine gave 40.2 g. (0.095 mole, 47.5%) of white rosettes, m.p. 198.5-199.5° (lit.[12] 194-196°). Concentrating the chlorobenzene filtrate gave an oil which could not be crystallized.

4-Phenylacetylphenyl Ether (2c).—The procedure was adapted from that of Dunn[12] and is essentially the same procedure given in the preceding paragraph. After cooling and pouring onto a mixture of 200 g. of ice and 100 g. of concentrated hydrochloric acid, the dark red reaction mixture changed to a pale yellow-green product. The solid was filtered and washed with 2% hydrochloric acid, once with 5% sodium hydroxide solution, once with water, pressed, and dried. The yellow-green product was recrystallized from 1 l. of benzene-alcohol (9:1) to give 57.0 g. of silky, white needles, m.p. 165-169°. A second crop (13.0 g.) from the mother liquor also melted at 165-169°. Final recrystallization from 700 ml. of benzene gave 59.5 g. (0.14 mole, 77%) of colorless, plate-like crystals, m.p. 169-170°.

***p,p'*-Diphenylglyoxalyldiphenylmethane (3b).**—To 4.04 g. (10.0 mmoles) of *p,p'*-diphenacetyldiphenylmethane in 50 ml. of absolute ethanol was added 5.3 g. (30.0 mmoles) of *p*-nitrosodiethylaniline (m.p. 85-86°) and the mixture refluxed for 5 hr. The ethanol was then distilled and 30 ml. of dilute hydrochloride acid (1:1) was added. The mixture was refluxed for 30 min., another 30-ml. portion of the dilute acid was added, and the reflux was continued for 30 min. The solution was then cooled, filtered, and the solid washed with two 50-ml. portions of cold absolute ethanol, affording 3.60-3.90 g. of impure, yellow-white product. This product was taken up in 65 ml. of acetone and chromatographed on Woelm acid alumina using acetone as the eluate. Concentration of the eluate to essential dryness, addition of 30 ml. of absolute ethanol, heating for 5 min., and then cooling, afforded 3.0-3.3 g. (6.93-7.63 mmoles, 69.3-76.3%) of white product, m.p. 143.0-144.5°. Recrystallization of 1.0 g. of this compound from 50 ml. of cyclohexane afforded 0.70 g. (70% recovery) of white flakes, m.p. 144.0-144.5°.

4,4'-Diphenylglyoxalylbiphenyl (3a).—In a 250-ml. flask a mixture of 3.9 g. (10 mmoles) of 4,4'-diphenacetylbiphenyl, 3.9 g. (0.035 mole) of gray selenium dioxide, and 100 ml. of acetic anhydride was refluxed for 5 hr. After cooling, the selenium metal was filtered on hardened filter paper, the precipitate washed with a few milliliters of acetic anhydride, and the combined filtrate and washings were warmed with 100 ml. of water. Upon cooling, a solid separated; this was taken up in 500 ml. of benzene and chromatographed on alumina (Alcoa F-20) using benzene as the eluent. Concentration of the eluate to approximately 100 ml. and cooling in ice, as 100 ml. of pentane was added with stirring, precipitate a yellow solid which was filtered and dried to give 3.25 g. of crude product, m.p. 180-190°. Recrystallization from 100 ml. of ethyl acetate afforded 2.70 g. (5.97 mmoles, 59.7%) of yellow crystals, m.p. 203.0-204.0°.

4-Phenylglyoxalylphenyl Sulfide (3d).—The conditions and ratio of reactants for this reaction are given previously to the point of purification by chromatography. Concentrations of the eluate to 75 ml., followed by cooling in an ice and water slurry,

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[10] O. Doebner, *Ann.*, **172**, 109, 117 (1874).

[11] C. V. Ferriss and E. E. Turner, *J. Chem. Soc.*, **117**, 1140, 1149, 1150 (1920).

[12] M. J. Dunn, M.S. thesis, Polytechnic Institute of Brooklyn, June, 1955.

while stirring the solution mechanically, as 100 ml. of pentane was added slowly, gave 26.5 g. (0.055 mole, 55%) of crude yellow material smelling of selenium, m.p. 75–80°. Recrystallization of the product from 100 ml. of hexane gave 24.0 g. (0.0532 mole, 53.2%) of bright yellow crystals, m.p. 90.0–91.6°.

4-Phenylglyoxalylphenyl Ether (3c).—The procedure for this reaction is essentially the same as for **3d**. The cooled, hydrolyzed mixture was extracted with chloroform, the chloroform solution washed with 25% sodium hydroxide solution, followed by water, dried over anhydrous sodium sulfate, and distilled. An oil separated which was still contaminated with red selenium metal. The oil was taken up in chloroform and chromatographed over Alcoa activated alumina (F-20), using chloroform as the eluent. Distillation of the solvent from the eluate gave an oil which solidified upon trituration with pentane, affording 33.0–35.4 g. (0.0759–0.0814 mole, 75.9–81.4%) of a yellow powder, m.p. 105–106.0°. Recrystallization of 3.0 g. of this product from 20 ml. of methanol gave 2.5 g. (83.0% recovery) of yellow crystals, m.p. 106.4–107.4°.

4-(3′-Phenylquinoxalin-2-yl)phenyl Ether.—A mixture of 1.0 g. (2.3 mmoles) of 4-phenylglyoxalylphenyl ether and 1.1 g. (10.2 mmoles) of *o*-phenylenediamine was heated on a hot plate at 110° for 15 min. Benzene (15 ml.) was added to the hot solution, followed by 9 ml. of pentane to precipitate 1.23 g. (2.1 mmoles, 92%) of tan crystals, m.p. 225–226.5°.

Anal. Calcd. for $C_{40}H_{26}N_4O$: N, 9.68. Found: N, 9.03.

3,3′-(4,4′-Biphenylene)bis[2,4,5-triphenylcyclopentadienone] (1a).—To a solution of 4.2 g. (20 mmoles) of benzyl ketone and 3.9 g. (9.5 mmoles) of **3a** in 100 ml. of absolute alcohol heated to incipient boiling, was added a solution of 0.30 g. (5.0 mmoles) of potassium hydroxide in 10 ml. of water, and the mixture was refluxed for 30 min. After cooling in ice the mixture was filtered and the solid was washed with 30 ml. of cold ethanol, leaving 8.5 g. of purple-black powder, m.p. 289–290°. Recrystallization from benzene–ethanol mixture gave 6.5 g. (8.4 mmoles, 89.1%) of purple-black crystals, m.p. 293.8–294.5°.

3,3′-(Thiodi-*p*-phenylene)bis[2,4,5-triphenylcyclopentadienone] (1d).—The reaction conditions and ratio of reactants are essentially those given previously. After 30 min. the refluxing was discontinued, the mixture was cooled, filtered, the precipitate washed twice with 95% ethanol, and then slurried with pentane, affording 13 g. (0.016 mole, 53.3%) of reddish brown crystals, m.p. 250–256° (Fisher-Johns melting point apparatus).

A mixture of 1 g. of this solid with 30 ml. of anhydrous ether was refluxed for 0.5 hr. The undissolved solid was filtered and again placed under reflux with 30 ml. of ether for 0.5 hr. The remaining solid, 0.8 g. (80% recovery) melted at 277.0–279.0° (Fisher-Johns).

4,4′-Methylenedi-*p*-phenylenebis(2,4,5-triphenyl-3-cyclopentadienone) (1b).—The conditions for this reaction are those given in the preceding paragraph, but the work-up was different. After cooling in ice the precipitate was filtered and washed with 5 ml. of absolute ethanol to give 9.0 g. of deeply colored solid, m.p. 178–180°. Recrystallization of 1.0 g. of material from 60 ml. of acetic acid and drying at 120° gave 0.43 g. of black needles, m.p. 240–243°. The solid was then recrystallized from a mixture of 11 ml. of benzene and 10 ml. of ethanol giving 0.35 g. of crystals, m.p. 246–247.7°. Another recrystallization from this benzene–ethanol mixture afforded 0.30 g. (0.38 mmole, 40.4%) of deeply colored black needles, m.p. 248.2–249.7°.

3,3′-(Oxydi-*p*-phenylene)bis[2,4,5-triphenylcyclopentadienone] (1c).—The reaction conditions are essentially those given in the preceding paragraph, but the work-up is different. After 15 min. of reflux, the reaction mixture was allowed to cool and was filtered to give 21.5 g. (79.4%) of red-brown crystals melting at 256.0–258.0°. Recrystallization of 1.0 g. of the sample from 75 ml. of acetonitrile gave 0.8 g. (80% recovery) of deep red crystals, m.p. 256.0–258.0°.

4-(2′,3′,5′,6′-Tetraphenyl)terphenylyl Ether (4c).—To 2.4 g. (3.0 mmoles) of triphenylcyclopentadienon-3-ylphenyl ether was added 2.0 g. (11.22 mmoles) of diphenylacetylene and the mixture stirred and heated in the absence of solvent and under nitrogen for 50 min. or until the refluxing ceased and a solid brown mass formed. The resulting solid was cooled, slurried with acetone, filtered, and dried to give 2.35 g. of crude product. Recrystallization from 100 ml. of tetralin afforded 2.00 g. (1.84 mmoles, 61.3%) of white crystals, m.p. 456–459°.

4-(2′,3′,5′,6′-Tetraphenyl)terphenylyl Sulfide (4d).—The ratio of reactants and reaction conditions are essentially those given in the preceding paragraph, except that the mixture was heated for 1 hr. The crude product, 1.40 g., was recrystallized from 50 ml. of benzene and afforded 1.20 g. (1.09 mmoles, 36.3%) of tan product, m.p. 442–446°.

Bis-(2′,3′,5′,6′-Tetraphenyl)terphenylylmethane (4b).—The ratio of reactants and reaction conditions are essentially the same as for **4c**, except that the mixture was heated for 10 min. This resulted in 2.8 g. of crude product of which 0.50 g. was recrystallized from 30 ml. of tetralin and afforded 0.43 g. of white crystalline powder, m.p. 440–444°.

2,′3′,5′,6′,2′′′′,3′′′′,5′′′′,6′′′′-Octaphenylsexiphenyl (4a).—Compound **1a** (1.6 g., 1.5 mmoles) and 1.0 g. (5.61 mmole) of diphenylacetylene were placed in a thick-walled tube, sealed under nitrogen, and the tube heated for 45 min. in a Wood's metal bath at 260°. At the end of this time the tube was cooled, and then opened, giving 1.75 g. of crude reddish white product, which after two recrystallizations from nitrobenzene afforded 1.30 g. (1.21 mmoles, 80.6%) of white crystalline powder, m.p. 440–442°.

Acknowledgment.—We wish to acknowledge the aid of Gary T. Hollander who, as part of his B.S. research (1960), carried out preliminary syntheses in the bistetracyclonyl sulfide series of compounds.