only one equivalent of Grignard reagent or one equivalent and an extra equivalent of magnesium bromide (generated by addition of extra magnesium and ethylene dibromide in original Grignard preparation) the yields of pure XI were considerably less and more than one acid was produced. The nature of the other acid, or acids, has not been studied.

o-(α-Isopropoxy-α-phenyl)toluic acid. When the Grignard reagent from 32 g. of bromobenzene in 110 ml. of ether was added to a stirred solution of 19.2 g. of X in 100 ml. of benzene and 50 ml. of ether, a complex separated at first which later dissolved to yield a deep red-brown solution. After refluxing for 15 min. the reaction mixture was treated as usual. A mixture of products was obtained no one of which was isolated in good yield. From the acid fraction 3.0 g. of colorless crystals, of o-(α-isopropoxy-α-phenyl)toluic acid, m.p. 83.5–85.0°, was obtained. The structure was established by analysis, infrared spectrum, and the fact that on heating in acetic acid–hydrobromic acid for 2 hr. an 84% yield of 3-phenylphthalide, m.p. and mixed m.p. 115–116°, was obtained.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.5; H, 6.7. Found[8]: C, 75.8; H, 6.6.

Oxidation of benzofurans, I, II *and* III. When a mixture of equivalent weights of each of the furans I, II, and III and of pure lead tetraacetate in tetrahydrofuran was shaken, the furans went into solution. By suitable work-up of the reaction mixtures the pure *o*-diaroylbenzenes were obtained in over 80% yields. 1,2-Dibenzoylbenzene,[4] m.p. 146–147°, and 1,2-dimesitoylbenzene;[6] m.p. 232.5–234.0°, had the reported properties. 1-Benzoyl-2-mesitoylbenzene, m.p. 157.5–158.5°, a new compound, recrystallized as colorless prisms from benzene-ethanol.

Anal. Calcd. for $C_{23}H_{24}O_2$: C, 84.1; H, 6.1. Found[8]: C, 84.2; H, 6.0.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ISRAEL INSTITUTE OF TECHNOLOGY]

Polycyclic Studies. I. Synthesis of Triphenylenes Through Diels-Alder Adducts[1]

A. MANDELBAUM[2] AND MICHAEL CAIS

Received October 4, 1960

The adducts obtained from the Diels-Alder addition of *p*-benzoquinones to bi(1-cyclohexen-1-yls) have been dehydrogenated over palladium-charcoal (30%) catalyst to form triphenylenes in satisfactory yields.

The interest in triphenylene (I) and its derivatives has been growing recently but few systematic studies of this type of compounds are available largely owing to difficulties in synthesis.[3] Recent work in these laboratories[4] suggested that the Diels-Alder addition of *p*-benzoquinone to bi(1-cyclohexen-1-yl) (II) might provide a simple method for building up the triphenylene nucleus. The addition of *p*-benzoquinone to II has been reported[5] to yield the adduct 1,4,5,6,7,8,9,10,11,12,13,16,17,18-tetradecahydrotriphenylene - 1,4 - dione[6] (IIIa) in low yields and it has been claimed[7] that four forms of a bis-adduct have been separated. There have been no reports, however, of the attempted transformation of adduct III into triphenylene. The successful results of this latter transformation form the subject of this paper and are summarized in chart 1.

The pinacols (IV) were obtained by slightly modifying the method reported[5] for the synthesis of IVa. Dehydration of the pinacols was carried out with phosphorus oxychloride in pyridine.[4a] These reaction conditions afforded reasonably high yields (> 75%) of the desired bicyclohexenyls II. Tables I and II summarize the data for the pinacols and bicyclohexenyls which have been prepared.

All our attempts failed to repeat the reported[5] preparation of adduct IIIa by treating *p*-benzoquinone and bi(1-cyclohexen-1-yl) in ethanol solution. Instead of IIIa we isolated in 17% yield the oxidized adduct Va. On the reasonable assumption that part of the quinone was used up in oxidizing the initially formed adduct IIIa, excess quinone was introduced in the above reaction with the result that the yield of the oxidized product Va was nearly doubled. Similar results were obtained in the reaction between *p*-toluquinone and bicyclohexenyls except in the case of bi(3,5-dimethyl-1-cyclohexen-1-yl) (IIe) which formed the normal adduct IIIe even when excess quinone was used. It seems reasonable to infer that the steric hindrance of the methyl groups in positions 5 and 12 prevents the removal of the hydrogens at positions 17 and 18.

By eliminating the use of solvent in the Diels-Alder reaction and using equimolar quantities of *p*-benzoquinone and bi(1-cyclohexen-1-yl) the normal adduct IIIa was obtained in 62% yield.

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[1] Taken from the Thesis submitted by A. Mandelbaum to the Senate of the Technion-Israel Institute of Technology, in partial fulfillment of the Degree of Master of Science, July 1960.

[2] American Chemical Society-Petroleum Research Fund Fellow, 1959–1960.

[3] For an excellent review of triphenylenes see C. M. Buess and D. D. Lawson, *Chem. Revs.*, **60**, 313 (1960).

[4] (a) D. S. Greidinger and D. Ginsburg, *J. Org. Chem.*, **22**, 1406 (1957); (b) Y. Strumza and D. Ginsburg, Abstracts Colloque International de Chimie Organique, Montpellier, September 1959; (c) Y. Altman and D. Ginsburg, *J. Chem. Soc.*, 466 (1959).

[5] E. B. Barnett and C. A. Lawrence, *J. Chem. Soc.*, 1104 (1935).

[6] The numbering of the triphenylene ring used in this article is the same as the one used in the recent review (ref. 3).

[7] H. J. Backer, J. Strating, and L. H. H. Huisman, *Rec. Trav. Chim.*, **58**, 761 (1939).

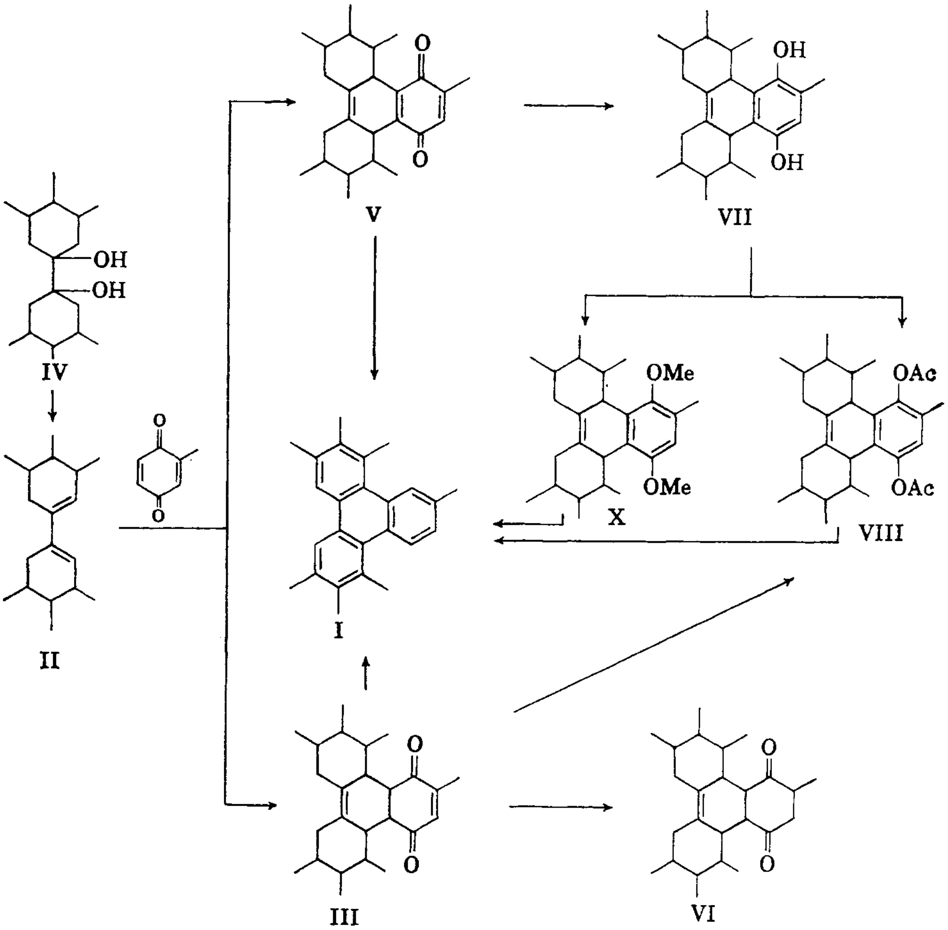
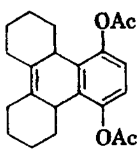
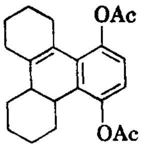


Table III summarizes the data for both the normal and the oxidized adducts which have been prepared.

The normal adducts III could be easily differentiated from the oxidized products V by their color (yellowish *vs.* brown), infrared absorption spectra (γ C=O 1682–1672 cm.$^{-1}$ *vs.* 1665–1651 cm.$^{-1}$) and chemical properties. Thus, whereas zinc–acetic acid reduction of the normal adducts III produced Δ^{14}-hexadecahydrotriphenylene-1,4-dione derivatives (VI), the same reaction conditions with the oxidized adducts V yielded the hydroquinone derivatives (VII). The latter are colorless, crystalline compounds which turn to yellow-brown on standing and readily form a diacetate (VIII) with acetic anhydride in pyridine. The same diacetate VIII was obtained when the adduct III was treated with acetic anhydride in pyridine. The fact that the ultraviolet spectrum of VIIIa is nearly identical with, and superimposable on, the spectrum of 1,4-diacetoxybenzene is taken as proof that the structure of VIIIa is as indicated and that there is no migration of the double bond to a conjugated position as shown in IX.



VIIIa



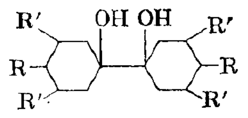
IX

Both the normal and the oxidized adducts (III and V, respectively) underwent hydrogenolysis, when dehydrogenated with 30% palladium-carbon catalyst, to produce the respective triphenylene derivatives. The reactions were carried out without solvent, at temperatures above 220°, and were completed within ten to twenty minutes in 40–70% yield.

Hydrogenolysis occurred also with the diacetoxy derivative VIIIa as well as with the dimethoxy compound X (obtained from the reaction of VIIa with dimethyl sulfate). Triphenylene, in yields of 46–74%, was the only product isolated from these reactions. However, dehydrogenation of 2-methyl-1,4-diacetoxy-5,6,7,8,9,10,11,12,13,16-decahydrotriphenylene (VIIIb) yielded 10% of 2-methyl-1,4-diacetoxytriphenylene (XI) in addition to 2-methyltriphenylene.

Attempts to use solvents, such as xylene, *p*-cymene and methylnaphthalene, did not give satisfactory results. Similarly, the use of sulfur in the dehydrogenation reaction introduced complications in the separation of the reaction products. Table IV summarizes the data for the triphenylenes prepared by the palladium-carbon dehydrogenation.

TABLE I. PREPARATION OF BICYCLOHEXANEDIOLS IV



IV

Ketone	Bicyclohexanediol	R	R′	Yield, %	M.P.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Oxygen, % Calcd.	Oxygen, % Found
Cyclohexanone	IVa	H	H	44[a]	128–131[b]							
4-Methylcyclohexanone	IVb	CH_3	H	28	112–115[c]							
4-Cyclohexylcyclohexanone	IVc	C_6H_{11}	H	29[a]	320–321[d]	$C_{24}H_{42}O_2$	79.50	79.23	11.68	11.43	8.83	9.01
4-Methoxycyclohexanone	IVd	OCH_3	H	22.5	155–157[e]	$C_{14}H_{26}O_4$	65.08	65.26	10.14	10.06	24.77	24.89
3,5-Dimethylcyclohexanone	IVe	H	CH_3	36.5	146–147[e]	$C_{16}H_{30}O_2$	75.53	75.60	11.89	11.83	12.58	12.80

[a] Prepared by the modified method, see Experimental. [b] Lit., ref. 5, m.p. 130°. [c] W. Ziegenbein, *Chem. Ber.*, **88,** 1787 (1955) reported m.p. 106–107°. [d] The crude reaction product which on dehydration gave 82% of the required diene IIc had m.p. 192–220°; repeated crystallizations from methylcyclohexane did not raise the melting point. The high melting isomer was obtained after three crystallizations from chloroform. [e] Recrystallized from methylcyclohexane.

The availability of bi(4-cyclohexyl-1-cyclohexen-1 yl) (IIc) prompted us to attempt the dehydrogenation of this compound. Quaterphenyl was obtained in 85% yield from this reaction.

The ultraviolet spectra of the new triphenylenes are shown in Figs. 1–3.

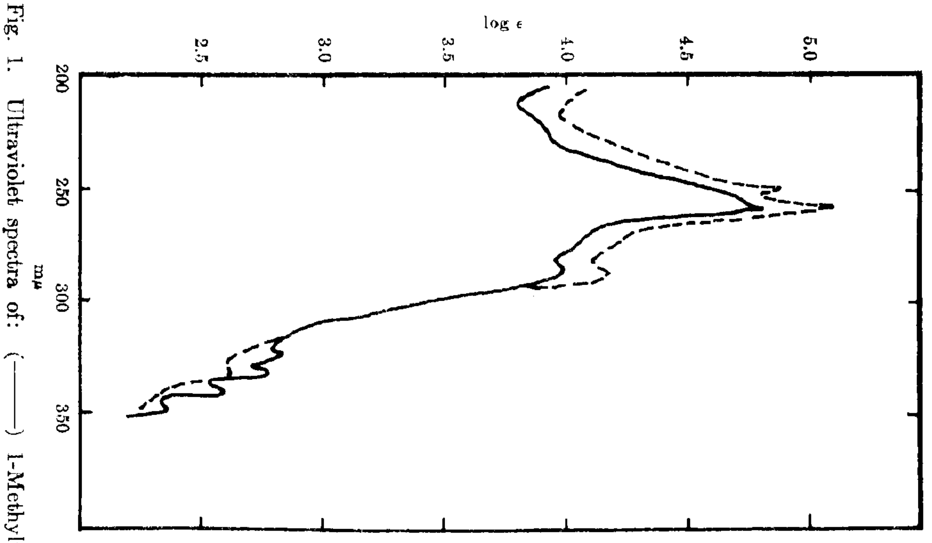


Fig. 1. Ultraviolet spectra of: (———) 1-Methyltriphenylene (in ethanol); (– – – –) 2-Methyltriphenylene (Id) (in ethanol)

In the region between 240–290 mμ the spectra of 2,7-dimethyltriphenylene (Ib) and 2,6,11-trimethyltriphenylene (Ie) are very similar in general appearance to the spectrum of 2-methyltriphenylene[8,9] (Id), with a bathochromic shift of 1–2 mμ for each additional methyl substituent. In the longer wave length region (between 300–350 mμ) the lower intensity bands (log ε < 3) of Ib and Ie are quite different from those of Id. The fine structure of the absorption bands in this region is absent from the spectrum of 2-methyltriphenylene but it appears in the spectra of 2,7-dimethyltriphenylene and 2,6,11-trimethyltriphenylene. This fact is of interest since the disappearance of the fine structure as well as other differences in the spectrum of 2-methyltri-

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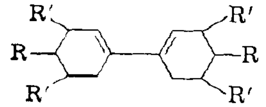
(8) M. Cais, D.Sc. Thesis, Israel Institute of Technology, Haifa, 1955.

(9) C. C. Barker, R. G. Emmersen, and J. D. Periam, *J. Chem. Soc.*, 1077 (1958).

TABLE II

PREPARATION OF BICYCLOHEXENYLS II



II

Bicyclo-hexenyl	R	R′	Yield, %	M.P., B.P.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
IIa	H	H	77	(67–68/0.2 mm.)[a]					
IIb	CH_3	H	80	(99–100/0.1 mm.)[b]					
IIc	C_6H_{11}	H	82	173–174.5[c]	$C_{24}H_{38}$	88.27	88.04	11.73	11.64
IId	OCH_3	H	75	(99–100/0.05 mm.)[d]					
IIe	H	CH_3	76	99–100[e] (88–90/0.06 mm.)	$C_{16}H_{26}$	88.00	87.84	12.00	11.77

[a] Lit., ref. 4a, b.p. 70–76°/0.05 mm. [b] Ziegenbein (see footnote[c] Table I) gives b.p. 103–105°/1 mm. [c] Recrystallized from benzene. [d] Used without further purification in the Diels-Alder reaction. [e] Recrystallized from ethanol.

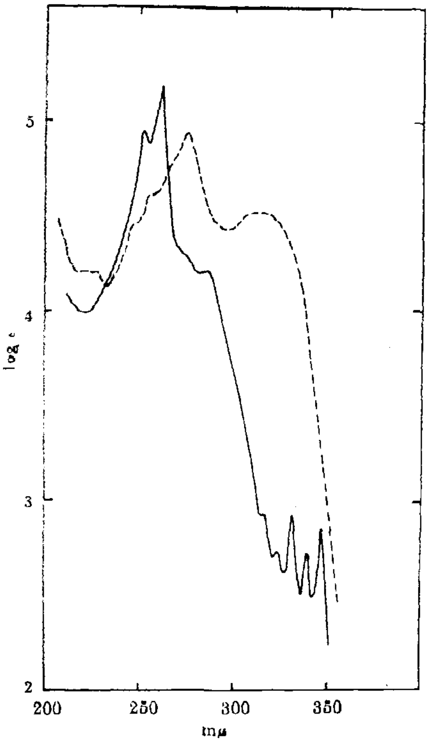


Fig. 2. Ultraviolet spectra of: (———) 2,7-Dimethyltriphenylene (Ib) (in ethanol); (- - - -) 2,7-Diphenyltriphenylene (Ic) (in cyclohexane)

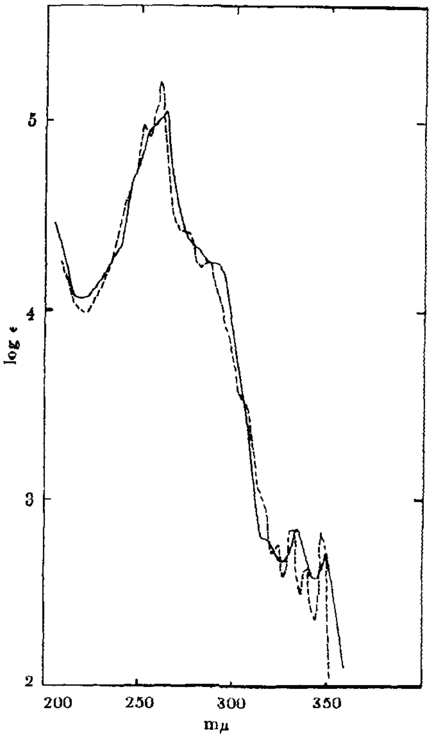


Fig. 3. Ultraviolet spectra of: (———) 1,4-Diacetoxy-2-methyltriphenylene (XI) (in ethanol); (- - - -) 2,6,11-Trimethyltriphenylene (Ie) (in ethanol)

phenylene as compared to that of 1-methyltriphenylene has been ascribed[8,9] to the possible steric effects of the methyl group in position 1.

The spectrum of 2,7-diphenyltriphenylene (Ic) shows two highly intense bands (λ_{max} 257 and 277 mμ, log ε 4.63 and 4.95) typical of the triphenylene system but in addition it also shows a highly intense band (log ε 4.54) at 313 mμ. It seems reasonable to ascribe this band to a substituted quaterphenyl chromophore since quaterphenyl itself absorbs at 300 mμ (log ε 4.59).[10] This highly intense band, which would be expected to mask any low intensity absorption in this region, prevents the possibility of comparing the low intensity absorption, in the 300–350 mμ region, of 2,7-diphenyltriphenylene with that of 2,7-dimethyltriphenylene.

The ultraviolet spectra of some of the Diels-Alder adducts and related compounds will be dealt with in a subsequent publication.

The scintillation properties of the newly prepared triphenylenes are currently being investigated. Also under investigation is the preparation of additional substituted triphenylenes through use of the active carbonyl functions of the reduced

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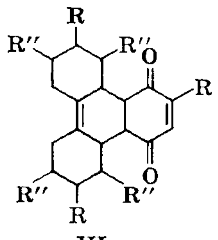
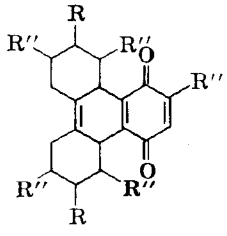
(10) A. E. Gillam and E. S. Stern, *Electronic Absorption Spectroscopy*, Edward Arnold, London, 1954, p. 210.

TABLE III

Adducts Obtained from Diels-Alder Reaction of Bicyclohexenyls with *p*-Quinones



III

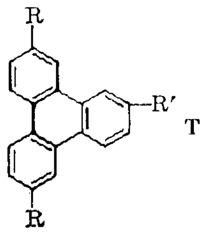


V

Diene	Quinone	Ratio Quinone: Diene	Reaction Solvent	Type of Product	R	R′	R″	Yield, %	M.P.	I.R. γ_{max}, cm.$^{-1}$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Oxygen, % Calcd.	Oxygen, % Found
IIa	*p*-Benzoquinone	1:1	—	IIIa	H	H	H	62	115.5–116.5[a,b]	1682	$C_{18}H_{22}O_2$	79.96	79.77	8.20	8.19	12.11	11.84
IIb	*p*-Benzoquinone	1:1	—	IIIb	CH_3	H	H	43	109.5–111[c]	1680	$C_{20}H_{26}O_2$	80.49	80.30	8.78	8.69	10.72	10.94
IIc	*p*-Benzoquinone	3:1	T.H.F.[d]	IIIc	C_6H_{11}	H	H	85	144–145.5[c]	1681	$C_{30}H_{42}O_2$	82.90	83.01	9.74	9.87	7.36	7.51
IId	*p*-Benzoquinone	1:1	—	IIId	OCH_3	H	H	60	131–132[c]	1682	$C_{20}H_{26}O_4$	72.70	72.72	7.93	7.98	19.37	19.51
IIe	*p*-Toluquinone	2:1	Ethanol	IIIe	H	CH_3	CH_3	59	145.5–146[c]	1678	$C_{23}H_{32}O_2$	81.13	81.16	9.47	9.28	9.44	9.40
IIa	*p*-Benzoquinone	1:1	Ethanol	Va	H	H	H	17	173–175[c]	1665	$C_{18}H_{20}O_2$	80.56	80.59	7.51	7.40	11.93	11.73
IIa	*p*-Benzoquinone	2:1	Ethanol	Va	H	H	H	25.5									
IIa	*p*-Toluquinone	1:1	Ethanol	Vc	H	CH_3	H	30	167–167.5[c]	1655	$C_{19}H_{22}O_2$	80.81	80.99	7.85	7.79	11.33	11.25
IIa	*p*-Toluquinone	2:1	Ethanol	Vc	H	CH_3	H	61									
IIa	*p*-Toluquinone	1:1	2-Propanol	Vc	H	CH_3	H	19.5									
IIa	*p*-Toluquinone	1:1	Methanol	Vc	H	CH_3	H	18									
IIb	*p*-Toluquinone	1:1	Ethanol	Vb	CH_3	CH_3	H	14.5	136.5–138[c]	1651	$C_{21}H_{26}O_2$	81.25	81.07	8.44	8.44	10.31	10.24
IIb	*p*-Toluquinone	2:1	Ethanol	Vb	CH_3	CH_3	H	17									

[a] Recrystallized from methanol. [b] Lit., ref. 5, m.p. 114°. [c] Recrystallized from ethanol. [d] Tetrahydrofuran.

TABLE IV.



I

TRIPHENYLENES FROM DEHYDROGENATION OVER 30% PALLADIUM-CARBON

Triphenylene	R	R′	Starting Material	Temperature of the Reaction	Time of the Reaction, Minutes	Yield, %	M.P.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Ia	H	H	IIIa	260–340	20	71	196–197[a,b]					
Ia	H	H	VIIIa	200–235	180	46.5						
Ia	H	H	X	220–260	30	74						
Ib	CH_3	H	IIIb	310–325	10	54.5	135.5–136[c]	$C_{20}H_{16}$	93.71	93.79	6.29	6.26
Ic	C_6H_5	H	IIIc	280–340	20	68	295.5–296[c]	$C_{30}H_{20}$	94.70	94.61	5.30	5.16
Id	H	CH_3	Vc	300–310	10	42	101–103[a]					
Ie	CH_3	CH_3	Vb	310–340	22	46	137.5–138.5[a,b,d]	$C_{21}H_{18}$	93.29	92.99	6.71	6.52

[a] White crystals from ethanol. [b] Purified by chromatography. [c] Recrystallized from benzene. [d] R. C. Hinton, F. G. Mann, and I. T. Millar, *J. Chem. Soc.*, 4704 (1958), give m.p. 128.5–129.5° for a pale brown material.

adducts VI, as well as other aspects of triphenylene synthesis.

EXPERIMENTAL

All melting points were measured in a capillary and are uncorrected.

4-Methoxycyclohexanone was prepared from *p*-methoxyphenol by a modification of the reported[11,12] method. Hydrogenation of the phenol was carried out at 4 atm. (instead of 85 atm.) and at 70° (instead of 120°) for 24 hr. *4-Methoxycyclohexanol* b.p. 110–112° (24 mm.) was obtained in 91% yield [lit.[11] b.p. 93–98° (12 mm.) in 75% yield]. The oxidation of 4-methoxycyclohexanol with potassium dichromate in sulfuric acid solution yielded 4-methoxycyclohexanone, b.p. 89–93° (24 mm.) [lit.[11] b.p. 76.5–77.5° (12 mm.)].

3,5-Dimethylcyclohexanone, b.p. 70–72° (20 mm.) [lit.[13] b.p. 178–180° (at atmospheric pressure)] was obtained from the potassium dichromate–sulfuric acid oxidation of 3,5-dimethylcyclohexanol. The latter compound b.p. 88–91° (20 mm.) was obtained in 90.5% yield from the hydrogenation (at 4 atm. and 70°) of 3,5-dimethylphenol.[14]

3,5-Dimethylcyclohexanone was also obtained in (86% yield) from the hydrogenation of 3,5-dimethyl-2-cyclohexen-1-one[15] over palladium-carbon (10%) in ethanol at 2 atm. and room temperature.

4-Cyclohexylcyclohexanone. *p*-Phenylphenol (50 g.) in glacial acetic acid (200 ml.) was hydrogenated over platinum oxide catalyst (1.5 g.) at 3–4 atm. for 12 hr. at room temperature. Filtration of the catalyst and removal of the solvent in a vacuum yielded a white solid (49 g.) which was used directly in the next step. To a solution of the crude hydrogenated product (98 g.) in acetic acid (300 ml.) was added, under stirring and cooling (ice bath), a solution of chromium trioxide (55 g.) in water (40 ml.) and acetic acid (500 ml.). The rate of addition was such that the temperature did not rise above 10°. After completing the addition (1.5 hr.) the cooling bath was removed and the mixture was allowed to stand overnight at room temperature. Methanol (100 ml.) was added and the solvents were then removed in vacuum to yield a green solid residue. This was acidified with 10% hydrochloric acid solution and extracted with ether (3 × 200 ml.). The ether extracts were washed with dilute hydrochloric acid solution, then with dilute sodium hydroxide solution, and then with water. After removal of the ether, the residue was distilled in vacuum to yield one fraction, (11 g.), b.p. 50–52° (0.07 mm.), which showed no carbonyl absorption in the infrared spectrum and a second fraction, (63.4 g.), b.p. 71–85° (0.08 mm.), which solidified on standing and showed a carbonyl absorption band in the infrared spectrum at 1710 cm.$^{-1}$ The second fraction was redistilled, b.p. 80–85° (0.08 mm.) and it solidified on standing, m.p. 38–40°, (lit.[16] reports m.p. 29.2° for 4-cyclohexylcyclohexanone).

Preparation of pinacols (IV), *of Table I*. The pinacols of Table I were prepared by the procedure reported[5] for the preparation of bi(1-hydroxycyclohex-1-yl) IVa.

In some cases, better yields were obtained when only catalytic amounts of mercuric chloride were used and

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(11) F. Hunziker, F. X. Muellner, and H. Schattegger, *Helv. Chim. Acta*, **38**, 1943 (1955).

(12) D. Papa, F. J. Villany, and H. F. Ginsberg, *J. Am. Chem. Soc.*, **76**, 4446 (1954).

(13) A. S. Bailey, N. Polgar, and R. Robinson, *J. Chem. Soc.*, 3034 (1953).

(14) T. W. Reinolds, J. M. Lamberti, H. H. Chanan, and P. M. Ordin, *Ind. Eng. Chem.*, **40**, 1751 (1948) report the use of 130 atm. pressure and a temperature of 200° for the hydrogenation of 3,5-dimethylphenol.

(15) *Org. Syntheses*, Coll. Vol. III, 317 (1955).

(16) H. E. Ungnade, *J. Org. Chem.*, **13**, 361 (1948).

TABLE V

ULTRAVIOLET ABSORPTION SPECTRA OF TRIPHENYLENES[a]

Compound	Solvent[b]		Absorptions										
2,7-Dimethyltriphenylene Ib	A	λ mμ			252	261	(276)[c]	288	317	325	332	340	348
		log ε			4.96	5.21	4.28	4.22	2.92	2.74	2.94	2.65	2.89
2,6,11-Trimethyltriphenylene Ie	A	λ mμ			253	262	(278)	289	(318)	325	334	341	349
		log ε			4.99	5.21	4.31	4.25	2.98	2.76	2.84	2.64	2.82
2,7-Diphenyltriphenylene Ic	B	λ mμ	222	229	257	277	313						
		log ε	4.21	4.20	4.63	4.95	4.54						
1,4-Diacetoxy-2-methyltriphenylene XI	A	λ mμ			(258)	264	(280)	(290)	(320)	336	352		
		log ε			4.97	5.06	4.35	4.25	2.77	2.85	2.71		

[a] Determined with Unicam, SP. 500 Spectrophotometer. [b] A = ethanol, B = cyclohexane. [c] ( ) inflection.

mercury metal was introduced in the reaction mixture. For example, to 0.51 mole of the ketone there were used 12 g. of mercury metal, 9 g. of coarse aluminum powder, and 0.2 g. of mercuric chloride.

Preparation of bi(1-cyclohexen-1-yls) (II) *of Table II.* The bicyclohexenyls of Table II with the exception of IId were prepared by the dehydration of the pinacols IV with phosphorus oxychloride in pyridine.[4a]

Bi(4-methoxy-1-cyclohexen-1-yl) (IId). The pinacol Id (1.5 g., 0.058 mole) in acetic anhydride (15 ml.) and glacial acetic acid (9 ml.) was refluxed for 3 hr. After cooling, water (25 ml.) was added and the solvents removed in vacuum. The residue (1.45 g.) was triturated with hexane to yield a white solid (0.18 g.) which was found to be starting material. The hexane filtrate was evaporated and the residue distilled in vacuum to yield 0.8 g. of a colorless liquid, b.p. 99–110° (0.05 mm.). This was used in the Diels-Alder reaction without any further purification.

Preparation of Diels-Alder adducts III of Table III. The general procedure for the Diels-Alder reaction of the bicyclohexenyls and *p*-quinones consisted of mixing equimolar amounts of the reactants and carefully heating the mixture to 55–65°. The heating was then stopped and the mixture allowed to stand at room temperature for about 72 hr. After triturating with methanol, the mixture was allowed to stand for several hours and then filtered to yield fairly pure yellow crystals. Generally one recrystallization was sufficient to yield analytically pure compounds. Because of the high melting point of the bicyclohexenyl Ic, the preparation of adduct IIIc was carried out in tetrahydrofuran. Attempts to use this solvent in the preparation of the other adducts were not successful.

Preparation of oxidized Diels-Alder adducts V of Table III. The use of solvents in the Diels-Alder reaction between bicyclohexenyls and *p*-quinones yielded the quinonoid adducts V and not III as reported.[5] The adduct III however was obtained in the reaction between IIe and *p*-toluquinone in ethanolic solution.

A solution of the bicyclohexenyl (0.01 mole) and the quinone (0.02 mole) in ethanol (10 ml.) was refluxed for 4 hr. On cooling brown crystals were deposited which were recrystallized generally from methanol.

The effects of different solvents and molar ratios of the reactants are summarized in Table III.

Triphenylenes of Table IV from palladium-carbon dehydrogenation reactions. The dehydrogenation reaction was carried out in a glass bulb (3–3.5 cm. in diameter) blown at the end of a 25–30 cm., 8 mm. diameter, glass tube. The open end of the glass tube was connected to a gas-collection apparatus. The Diels-Alder adduct (0.002 mole) and the catalyst 30% palladium-carbon (20 mg.) were introduced into the bulb through a long stemmed funnel, without any solvent. The bulb was introduced into a metal bath, preheated to about 200°, and then the temperature of the bath was raised until a rapid stream of hydrogen was evolved. The bath was kept at this temperature until the evolution of gas slowed down and then the temperature was raised another 20–30° for about 3–4 min., when the gas evolution stopped altogether. The whole operation took between 10–20 min. The amount of hydrogen collected was a good indication of the completeness of the reaction.

The reaction mixture was cooled, hot benzene (10 ml.) was added and the benzene solution filtered off. This operation was repeated two or three times and the benzene washings collected and concentrated to a small volume (~3 ml.). Addition of a little ethanol induced precipitation of the dehydrogenated product. Filtration and one recrystallization yielded fairly pure compounds in yields between 42–74%.

Further purification for analytical samples could be effected by chromatography over basic alumina and elution with hexane-benzene mixtures.

1,4-Diacetoxy-2-methyltriphenylene (XI). When 1,4-diacetoxy - 2 - methyl - 5,6,7,8,9,10,11,12,13,16 - decahydrotriphenylene, VIIIb, (0.5 g.) was dehydrogenated as described above with 30% palladium-carbon (0.15 g.) at 230–240° for 50 min., there was evolved 120 ml., (4 moles) of hydrogen. After extracting the mixture twice with hot benzene and filtering off the catalyst the benzene washings were evaporated. The residue was triturated with hot hexane and the mixture allowed to cool. White crystals, (50 mg.) m.p. 153–155°, separated. One recrystallization from methanol yielded the analytical sample, m.p. 164–164.5°.

Anal. Calcd. for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found: C, 77.00; H, 4.98.

The infrared spectrum showed carbonyl absorption at 1758 cm.$^{-1}$

In another experiment, in an attempt to separate the crude reaction mixture by chromatography over neutral alumina, elution with hexane produced 26% yield of 2-methyltriphenylene, Id, m.p. 101–103° (lit.[17] m.p. 102.6–103.6°).

Further elution of the column did not yield any diacetoxytriphenylene but yielded fractions whose infrared absorption spectra showed the quinonoid absorption band at 1655 cm.$^{-1}$ It is likely that the alumina caused hydrolysis of the acetoxy groups followed by air oxidation of the resulting phenols.

1,2,3,4,5,6,7,8,9,10,11,12,13,16,17,18-Hexadecahydrotriphenylene-1,4-dione (VI). To a stirred solution of 1,4,5,6,

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(17) L. F. Fieser and L. M. Joshel, *J. Am. Chem. Soc.*, **61**, 2958 (1939).

7,8,9,10,11,12,13,16,17,18 - tetradecahydrotriphenylene - 1,4-dione, IIIa, (6 g., 0.022 mole) in glacial acetic acid (80 ml.) zinc powder (17 g.) was added in small amounts. Heat was evolved in the reaction and after stirring for 10 min., the reaction mixture was filtered. The precipitate was washed twice with acetic acid and the filtrates were poured into water (1.5 l.), with vigorous stirring. The white precipitate which separated was filtered, washed several times with water and dried for 4 days in a vacuum desiccator over calcium chloride and potassium hydroxide pellets. There was obtained a white powder (6.05 g., 100%) m.p. 116–118°. One crystallization from hexane produced the analytical sample, m.p. 116–118°.

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88; O, 11.75; Found: C, 79.39; H, 8.63; O, 11.83.

The infrared spectrum shows the carbonyl absorption band at 1720 cm.$^{-1}$

1,4-Dihydroxy-5,6,7,8,9,10,11,12,13,16-decahydrotriphenylene (VIIa). Zinc powder (25 g.) was added to a stirred, hot solution of 1,4,5,6,7,8,9,10,11,12,13,16-dodecahydrotriphenylene-1,4-dione, Va (5 g., 0.185 mole) in glacial acetic acid (200 ml.). When the temperature of the reaction mixture reached 90° another 25 g. of zinc powder was added and the mixture stirred, under reflux, for 30 min. After cooling and filtration, the precipitate was washed with acetic acid and the filtrates evaporated in vacuum. The brown residue was dissolved in boiling methylcyclohexane (250 ml.) treated with activated charcoal, the filtered solution concentrated to 100 ml. and cooled to deposit a pinkish precipitate. One crystallization from methylcyclohexane produced a grayish solid (2.1 g.) m.p. 139–143°. Repeated crystallizations from methylcyclohexane did not raise the melting point. Sublimation in high vacuum gave the analytical sample, m.p. 170–171.5°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20; O, 11.84. Found: C, 80.15; H, 8.29; O, 12.08.

1,4-Diacetoxy-5,6,7,8,9,10,11,12,13,16-decahydrotriphenylene (VIIIa). (a) A mixture of 1,4-dihydroxydecahydrotriphenylene, VIIa (0.2 g.), acetic anhydride (3 ml.), and pyridine (5 ml.) was allowed to stand overnight at room temperature. The mixture was then poured into iced water and the yellowish precipitate (0.1 g., 38%) collected had m.p. 149–154°. One recrystallization from methanol gave crystals with m.p. 159–160° (lit.[5] m.p. 161°). The infrared spectrum showed the aromatic acetate[18] carbonyl absorption at 1756 cm.$^{-1}$

The ultraviolet spectrum showed a maxima at 264 mμ (log. ϵ 2.65) and was identical to that of 1,4-diacetoxybenzene.[19]

(b) A solution of the adduct IIIa (3 g.) in pyridine (27 ml.) and acetic anhydride (15 ml.) was allowed to stand at room temperature for 23 hr. After the addition of ice water (250 ml.) the mixture was extracted twice with ether, the ether solution washed several times with dilute hydrochloric acid solution and then with water, dried and evaporated. The oily residue was triturated with pentane to give a white solid (1.9 g., 49%) m.p. 156–158°. One recrystallization from methanol raised the m.p. to 159–160°. The infrared spectrum was identical with that of the compound obtained by the method (a).

1,4-Diacetoxy-2-methyl-5,6,7,8,9,10,11,12,13,16-decahydrotriphenylene (VIIIb). A solution of 2-methyl-1,4,5,6,7,8,9,10,11,12,13,16-dodecahydrotriphenylene-1,4-dione, Vc (5 g.), in acetic acid (150 ml.) was treated with zinc powder (50 g.) as described for VIIa. After work-up as before and crystallization from methylcyclohexane was obtained 3.5 g. (70%) of *1,4-dihydroxy-2-methyl-5,6,7,8,9,10,11,12,13,16-decahydrotriphenylene* (VIIb), m.p. 100–104°. The dihydroxy derivative, VIIb (4 g.), in pyridine (24 ml.) and acetic anhydride (16 ml.) was allowed to stand overnight and then the reaction mixture was worked up as for VIIIa to obtain 4 g. (77.5%) of the diacetoxy derivative as a white solid, m.p. 116.5–117.5°. One recrystallization from hexane gave the analytical sample, m.p. 118.5–119°.

Anal. Calcd. for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66; O, 17.37. Found: C, 75.10; H, 7.52; O, 17.32;

The infrared spectrum showed the carbonyl absorption at 1758 cm.$^{-1}$

*1,4-Dimethoxy-5,6,7,8,9,10,11,12,13,16-*decahydrotriphenylene (X). Dimethyl sulfate (10 ml.) was added dropwise to a stirred, refluxing solution of VIIa (1 g.) in dioxane (15 ml.) and 20% potassium hydroxide solution (15 ml.). The black-colored solution was stirred for another hour at 100°, then diluted with water (100 ml.) and cooled. After three extractions with ether, the ether solution was washed with dilute potassium hydroxide solution, then with dilute hydrochloric acid, and then with water. Drying [magnesium sulfate] and evaporation of the ether yielded a yellow-brown solid (0.5 g.) which, after sublimation, gave a yellow solid m.p. 156–157°. Resublimation produced the analytical sample, white crystals, m.p. 157.5–158°.

Anal. Calcd. for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78; O, 10.72. Found: C, 80.61; H, 8.64; O, 10.52.

Quaterphenyl. Bi(4-cyclohexyl-1-cyclohexen-1-yl), IIc (0.1 g.), was dehydrogenated over 30% palladium-carbon catalyst (0.05 g.) at 330° for 15 min. and then at 350° for another 15 min. when the evolution of hydrogen stopped. The reaction mixture was extracted several times with boiling toluene. The combined toluene extracts were concentrated until a solid began to crystallize. White, lustrous crystals (80 mg., 85%) were obtained m.p. 310–312°; lit.[20] reports for quaterphenyl m.p. 310°.

Acknowledgment. It is a pleasure to thank Prof. D. Ginsburg who suggested to us the Diels-Alder approach to the synthesis of triphenylenes, and Prof. E. D. Bergmann who interested one of us (M. C.) in the triphenylene problem.

This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

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