4-N,N-Dimethylamino-7-bromohydrindene.—4-Amino-7-bromohydrindene (2.1 g., 0.01 mole) and 5.2 g. (0.1 mole) of 88% formic acid were heated in a 50-ml. erlenmeyer flask fitted with a reflux condenser on a steam-cone for two hours. Two grams of 40% aqueous formaldehyde was added and the heating was continued for 14 hours. Concentrated hydrochloric acid (2.5 ml.) was added and the reflux condenser was removed to permit the volatile material (excess formaldehyde and formic acid) to escape. The resulting mixture was removed from the steam-cone, diluted with water and made alkaline. The product was extracted with ether and dried over magnesium sulfate. Distillation of the ether residue at reduced pressure through a 30-cm. spiral wire column yielded 1.25 g. (52%) of a colorless liquid, b.p. 90–92 (2 mm.), n^{25}D 1.5914.

4-N,N-Dimethylamino-7-bromohydrindene.—To 5.8 g. (0.02 mole) of 4-amino-5,7-dibromohydrindene dissolved in 80 ml. of glacial acetic acid contained in a 500-ml. flask fitted with a reflux condenser and an off-set dropping funnel were added 45 g. of amalgamated mossy zinc and 15 ml. of 40% aqueous formaldehyde. Concentrated hydrochloric acid (10 ml.) was added and the gray mixture was heated to reflux temperature. An additional 75 ml. of concentrated hydrochloric acid was added during a period of 11 hours. After a reflux period of 24 hours, the acidic solution was decanted from the zinc, cooled and treated with sufficient aqueous sodium hydroxide to dissolve the zinc hydroxide which formed. The product was extracted with a benzene–ether mixture. After the organic layer had been dried over magnesium sulfate, the solvent was removed, and the residue was distilled at reduced pressure yielding 3.8 g. (79%) of colorless liquid; n^{25}D 1.5912. Redistillation of this material through a 30-cm. spiral wire column gave an analytical sample of colorless 4-N,N-dimethylamino-7-bromohydrindene, b.p. 93–93.5° (2.5 mm.), n^{25}D 1.5913.

Anal. Calcd. for $C_{11}H_{14}NBr$: C, 55.01; H, 5.88. Found: C, 55.18; H, 5.91.

4-N,N-Dimethylaminohydrindene-7-carboxylic Acid.—Lithium (0.71 g., 0.1 g. atom) was added to 50 ml. of anhydrous ether contained in a 500-ml. three-necked flask fitted with a Trubore stirrer, a dropping funnel and a reflux condenser. A solution of 10.95 g. (0.046 mole) of 4-N,N-dimethylamino-7-bromohydrindene in 50 ml. of dry ether was added during a period of 25 minutes with vigorous stirring. The reaction started within a few minutes. The dark mixture was stirred at reflux temperature for 45 minutes, then was poured on crushed Dry Ice. Following evaporation of the Dry Ice, the ether residue was shaken with 200 ml. of 1% aqueous potassium hydroxide. Acidification of the aqueous layer (*p*H 6) resulted in the separation of 6.1 g. of colorless solid. A second crop of 0.6 g. of reddish solid was obtained by concentration of the filtrate, ether extraction and removal of the solvent. Sublimation of the combined crops at 175° (5 mm.) yielded 6.2 g. (66%) of colorless solid, m.p. 182.5–184°. Two recrystallizations from nitromethane gave an analytical sample of 4-N,N-dimethylaminohydrindene-7-carboxylic acid as colorless needles, m.p. 183–183.8°.

Anal. Calcd. for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; neut. equiv., 205.2. Found: C, 69.94; H, 7.54; neut. equiv., 205.1.

Ethyl 4-N,N-Dimethylaminohydrindene-7-carboxylate.—To 8.2 g. (0.04 mole) of 4-N,N-dimethylaminohydrindene-7-carboxylic acid in 150 ml. of anhydrous ether at 0° was added sufficient ethereal diazoethane (approximately 0.05 mole) to impart a permanent yellow coloration to the solution. After 20 hours, the solvent was removed at reduced pressure and the yellow residue was distilled through a 30-cm. spiral wire column. The yield of colorless liquid, b.p. 132.5–135° (0.5 mm.), n^{25}D 1.5716, was 8.1 g. (87.1%). Redistillation gave material with n^{25}D 1.5716. This liquid was dissolved in anhydrous ether and shaken with anhydrous potassium carbonate. The potassium carbonate was separated by filtration. Removal of the solvent at reduced pressure gave 4-N,N-dimethylamino-7-carbethoxyhydrindene as a colorless solid. Recrystallization from absolute ether using a Dry Ice–acetone bath gave the ester, m.p. 44.5–45.5°, n^{25}D 1.5717.

Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.03; H, 8.32; N, 6.25.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Tetraarylcyclopentadienes[1]

BY LOUIS MEHR,[2] ERNEST I. BECKER[3] AND PAUL E. SPOERRI

RECEIVED JULY 19, 1954

A number of symmetrically substituted 1,2,4,5-tetraarylpentane-1,5-diones have been synthesized by coupling substituted α-phenylacetophenones with formaldehyde in a base-catalyzed reaction. Michael addition of substituted α-phenylacetophenones to α-phenylacrylophenone produced unsymmetrically substituted 1,5-diones. Conversion of the 1,5-diketones to tetraarylcyclopentadienes was effected *via* reductive cyclization with zinc in acetic acid to the corresponding 1,2,3,5-tetraarylcyclopentane-1,2-diols followed by their dehydration, or in the same steps, but without isolation of the diols.

Introduction

It is the purpose of this work to describe the synthesis of a number of 2,3,4,5-tetraarylcyclopentadienes which were desired in order to test their behavior as organic semi-conductors in the xerographic process. The synthesis of these compounds starts with the reductive cyclization of 1,5-diketones. Thus, the synthesis of the 1,5-diketones is the key step in the sequence. This leads to a division of the experimental work into the synthesis of 1,5-diketones, and their reductive cyclization to cyclopentanediols followed by their dehydration to cyclopentadienes or reductive cyclization and dehydration directly to cyclopentadienes.

Symmetrically Substituted 1,5-Diketones.—The symmetrical 1,5-diketones were synthesized by coupling two molecules of an α-phenylacetophenone with formaldehyde according to Wislicenus and Carpenter[4] as modified by Ziegler and Schnell[5] (equation 1). The α-phenylacetophenones were prepared according to literature procedures.

The yield of the 1,5-diketones varied from 32–94%. Table I summarizes most of the data. Typical procedures are given in the Experimental part.

Unsymmetrically Substituted 1,5-Diketones.—The direct adaptation of the procedure of Wislice-

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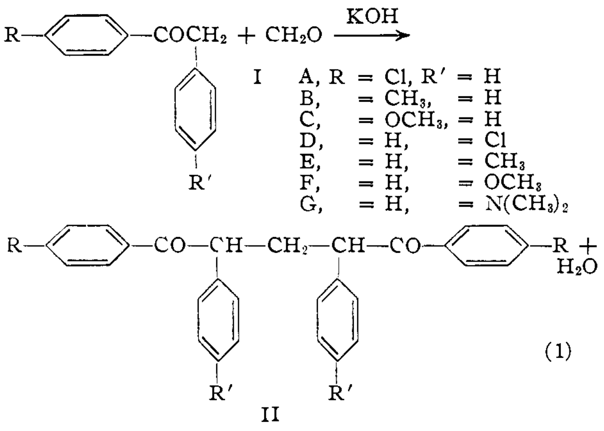
(1) This investigation was sponsored by the Photographic Branch of the Signal Corps Engineering Laboratory under Contracts W36-039 sc 44483 and DA36-039 sc 15326 and was presented at the Meeting-in-Miniature of the Metropolitan Long Island Subsection of the New York Section, Inc., of the American Chemical Society, Brooklyn, New York, March, 1953.

(2) Taken from the Dissertation presented by L. M. to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the Ph.D. degree.

(3) To whom inquiries should be sent.

(4) J. Wislicenus and H. Carpenter, *Ann.*, **302**, 223 (1898).

(5) K. Ziegler and B. Schnell, *ibid.*, **445**, 266 (1925).



I A, R = Cl, R' = H
B, = CH_3, = H
C, = OCH_3, = H
D, = H, = Cl
E, = H, = CH_3
F, = H, = OCH_3
G, = H, = $N(CH_3)_2$

II

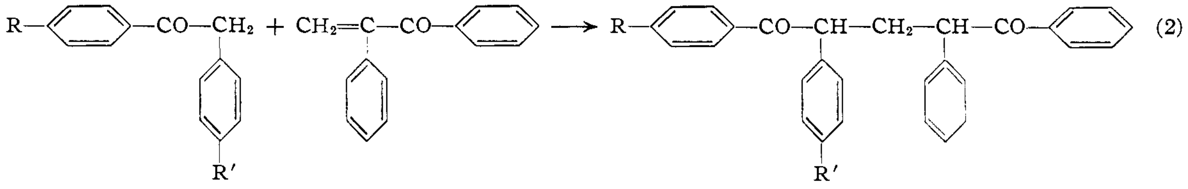
TABLE I

SYMMETRICALLY SUBSTITUTED TETRAARYL-1,5-DIKETONES (II-A-G)

	Starting materials				Products, II				Analyses, %			
									Carbon		Hydrogen	
I-	α-Phenylacetophenone, g.	Formaldehyde,[a] g.	Potassium hydroxide, g.	Methanol, ml.	M.p., °C.	Yield g.	Yield %	Empirical formula	Calcd.	Found	Calcd.	Found
A	30.0	1.96	7.5	500	175.5–178	28.8	94[b]	$C_{29}H_{22}Cl_2O_2$	73.57	73.51	4.68	4.62[c]
B	30.0	2.11	7.6	400	132 –133	26.4	86	$C_{31}H_{28}O_2$	86.08	85.78	7.53	6.52
C	30.0	1.96	7.0	500	148.5–149.5	25.1[d]	82	$C_{31}H_{28}O_4$	80.15	79.94	6.07	6.14
D	15.0	0.96	3.65	300	170.5–171.5	13.7	90	$C_{29}H_{22}Cl_2O_2$	73.57	73.72	4.68	4.81[e]
E	5.0	.36	1.35	75	160 –161	3.80	74[f]	$C_{31}H_{28}O_2$	86.08	86.00	6.52	6.61
F	8.0[g]	.53	1.99	200	148 –149	7.58	92[h]	$C_{31}H_{28}O_4$	80.15	79.95	6.07	6.14
G	15.0[h,i]	.96	3.48	400	210 –211[j]	4.05	32	$C_{33}H_{34}N_2O_2$	80.78	80.58	6.99	7.20[k]

[a] The corresponding quantities of Formalin (37% by weight of CH_2O) were employed. [b] As the unrecrystallized product, m.p. 174–177°. [c] *Anal.* Calcd. for $C_{29}H_{22}Cl_2O_2$: Cl, 14.98. Found: Cl, 14.84, 14.93. [d] A portion was converted to the di-2,4-dinitrophenylhydrazone, m.p. 236–237°. *Anal.* Calcd. for $C_{43}H_{36}N_8O_{10}$: C, 62.61; H, 4.40; N, 13.59. Found: C, 62.70; H, 4.43; N, 13.72. [e] *Anal.* Calcd. for $C_{29}H_{22}Cl_2O_2$: Cl, 14.98. Found: Cl, 15.12, 15.17. [f] As the unrecrystallized product, m.p. 157–159°. [g] After stirring for one hour at 45° the reaction mixture was shaken mechanically for 24 hr. at room temperature. [h] As the unrecrystallized product. [i] Forty-five minutes after the reaction started, incipient clouding took place in the body of the solution although starting material still was present. Decanting the reaction mixture allowed 2.45 g. of starting material to be recovered. [j] From ethyl acetate. Acetonitrile gave m.p. 209.5–210.5°. [k] *Anal.* Calcd. for $C_{33}H_{34}N_2O_2$: N, 5.71. Found: N, 5.97.

nus and Carpenter[4] and Ziegler and Schnell[5] did not appear promising for the synthesis of unsymmetrically substituted 1,5-diketones since from any pair of different α-phenylacetophenones, three products could be formed. Consideration of one of several routes for the reaction pointed toward the formation of α-phenylacrylophenone as an intermediate. This would result from condensation of α-phenylacetophenone with formaldehyde.



I

III

A, R = Cl, R' = H
B, = CH_3, = H
C, = OCH_3, = H
D, = H, = Cl
E, = H, = CH_3
H, = H, = H
I, = H, = $N(CH_3)_2$

An argument for this course is the well-known fact that aldols are readily dehydrated by strong bases.[6–8] In principle, then, the synthesis of unsymmetrically substituted 1,5-diketones would take place by a Michael addition of a substituted α-phenylacetophenone to α-phenylacrylophenone.[9]

α-Phenylacrylophenone, which was not known when this work had been completed, was synthesized by dehydrating α-methylbenzoin which was first prepared by the inverse addition of methylmagnesium iodide to benzil.[10] When equimolar quantities of α-phenylacrylophenone and α-phenylacetophenone were treated in methanol with a catalytic quantity of potassium hydroxide, the expected 1,5-diketone, II (R = R' = H), was formed. This reaction was extended to include α-phenylacetophenones substituted with methyl, chloro, methoxyl or dimethylamino groups (equation 2) and Table II.

The diketone 2-(4'-anisyl)-1,4,5-triphenylpentan-1,5-dione was not prepared according to this procedure because the cyclic diene ultimately to be realized from it had already been reported by Dilthey, *et al.*[11] Their starting diketone was 3-(4'-anisyl)-1,2,5-triphenylpentan-1,5-dione (III-J), prepared with difficulty by the Michael addition of α-phenylacetophenone to 4-methoxychalcone. Replacing the sodium methoxide employed by them with a lower concentration of potassium hydroxide

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(6) C. Loewig and S. Weidemann, *J. prakt. Chem.*, **21**, 54 (1840).

(7) H. Weidenbusch, *Ann.*, **66**, 152 (1848).

A. Lieben, *ibid.*, Supplementary vol. 1, 117 (1861).

(9) Although this particular Michael reaction has not been reported, analogous reasoning has been reported at least sixty years ago, E. Knoevenagel, *ibid.*, **281**, 25 (1894).

(10) R. Roger, *J. Chem. Soc.*, 518 (1925).

(11) W. Dilthey, O. Trösken, K. Plum and W. Schommer, *J. prakt. Chem.*, **141**, 331 (1934).

TABLE II

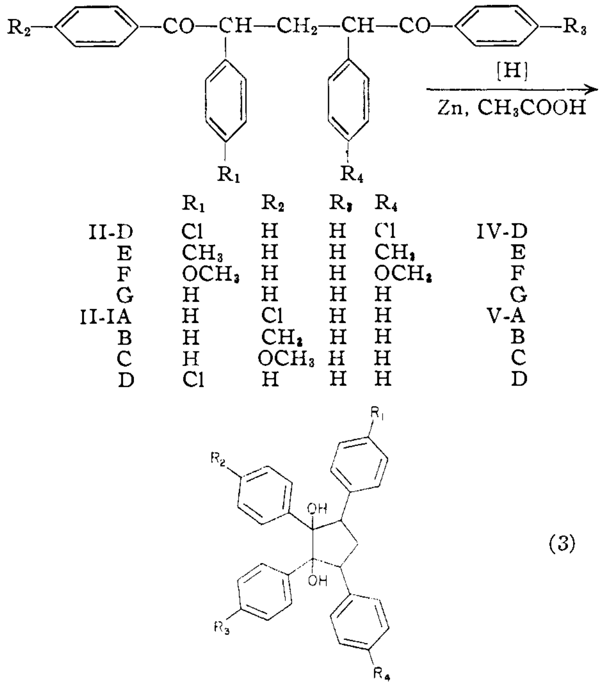
UNSYMMETRICALLY SUBSTITUTED TETRAARYL-1,5-DIKETONES

	Starting materials					Products, III				Analyses, %			
	α-Phenylacetophenone, g.	α-Phenylacrylophenone, g.	Potassium hydroxide, g.	Methanol, ml.	Time, hr.		Yield			Carbon		Hydrogen	
I-						M.p., °C.	G.	%	Empirical formula	Calcd.	Found	Calcd.	Found
A	5.0	4.5	0.65	120	72	152.5–154	8.12	88[a]	$C_{29}H_{23}ClO_2$	79.34	79.31	5.28	5.33[b]
B	5.0	4.9	.72	175	72	115– 116.5	8.37	85[c]	$C_{30}H_{26}O_2$	86.09	86.10	6.26	6.41
C	5.0	4.6	.67	100	36	146.5–147.5	7.08	74	$C_{30}H_{26}O_3$	82.92	83.20	6.03	5.73
D	5.0	4.5	.65	120	48	117 –118[d]	7.25	77[e]	$C_{29}H_{23}ClO_2$	79.34	79.49	5.28	5.34[f]
E	5.0	4.9	.72	120	48	118.5–120[g]	7.5	77[h]	$C_{30}H_{26}O_2$	86.09	85.51	6.26	6.42
H	0.47	0.5	.09	10	3.5	148 –149[i]	0.78	80	$C_{29}H_{24}O_2$	86.11	86.06	5.98	6.11
I	5.0	4.3	1.14	120	72	187.5–188.5[g]	8.0	86[j]	$C_{31}H_{29}NO_2$	83.19	83.02	6.53	6.36[k]

[a] Yield is for unrecrystallized product, m.p. 149–151.5°. [b] *Anal.* Calcd. for $C_{29}H_{23}ClO_2$: Cl, 8.07. Found: Cl, 8.29. [c] Yield is for unrecrystallized product, m.p. 114–116.5°. [d] Recrystallized from glacial acetic acid. [e] Yield is for unrecrystallized product, m.p. 112–115°. [f] *Anal.* Calcd. for $C_{29}H_{23}ClO_2$: Cl, 8.07. Found: Cl, 8.22. [g] Recrystallized from acetonitrile. [h] Yield is for unrecrystallized material, m.p. 113.5–116.5°. [i] Does not depress an authentic sample prepared according to footnotes 4 and 5. [j] Yield is for unrecrystallized material, m.p. 177–183°. [k] *Anal.* Calcd. for $C_{31}H_{29}NO_2$: N, 3.12. Found: N, 3.41.

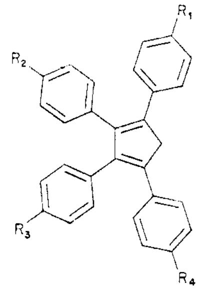
both improved the yield and the ease of isolation of the product.[12]

p-Substituted-1,2,3,5-tetraphenylcyclopentane-1,2-diols and p-Substituted-2,3,4,5-tetraphenylcyclopenta-2,4-dienes.—Wislicenus and Carpenter[4] and later Ziegler and Schnell[5] reductively cyclized II-G to IV-G, the corresponding diol, using zinc in acetic acid. This general procedure as used here successfully converted a number of 1,5-diketones to the cyclic diols in from 11–64% yield (equation 3). These diols were then dehydrated to the corresponding dienes. Alternatively the diols were not isolated from the crude reaction mixture, but dehydrated directly to the dienes (equation 4).



	R_1	R_2	R_3	R_4	
II-D	Cl	H	H	Cl	IV-D
E	CH_3	H	H	CH_3	E
F	OCH_3	H	H	OCH_3	F
G	H	H	H	H	G
II-IA	H	Cl	H	H	V-A
B	H	CH_3	H	H	B
C	H	OCH_3	H	H	C
D	Cl	H	H	H	D

(3)



(4)

The proof of structure of the dienes (series VI- and VII-) synthesized here was unequivocally established by condensing them with *p*-nitrosodimethylaniline and then, generally without isolation of the anils, hydrolyzing them to the corresponding tetracyclones (series X- or XI-, Table V). In two cases (VI-C and VII-J) the intermediate, purple dimethylaminoanils (VIII-C and IX-J, respectively) were isolated and characterized. Mixture melting points with authentic tetracyclones previously prepared by condensing a benzil and a benzyl ketone were not depressed. The dienes were further characterized by their bright, blue-white fluorescence in solution or in the solid state.

Returning to their xerographic testing, all of the dienes synthesized exhibited from "fair" to "good" xerographic behavior. These data are to be published elsewhere.

Experimental[13]

Symmetrically Substituted 1,5-Diones

The 1,5-Bis-(4′-R-phenyl)-2,4-diphenylpentan-1,5-diones (Table I).—The substituted 4-R-α-phenylacetophenone was dissolved or suspended in methanol at 45° and the formalin solution was added with vigorous stirring. Immediately thereafter, a solution of potassium hydroxide, dissolved in 5 ml. of water was added and stirring was maintained for 1 hr. The order of addition was immaterial. The solution became yellow, the chlorophenyl analog intensely so. After shaking the reaction mass mechanically overnight at room temperature, it was filtered and the mother liquor was neutralized with acetic acid. Approximately half the solvent was removed by distillation at atmospheric or at reduced pressure. Chilling usually gave a second crop. The two

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(12) As an explanation for the poor yield, Dilthey suggested that an isomeric 1,4-diketone, 2-(4′-methoxybenzyl)-1,2,4-triphenylbutan-1,4-dione, was formed. Conceivably such a product could be formed by initial hydrolysis of the chalcone and then condensation of 4-methoxybenzaldehyde with a α-phenylacetophenone and followed by the addition of another molecule of α-phenylacetophenone, but with the new C–C bond forming α to the carbonyl group of the acrylophenone; this is unlikely.

(13) Melting points are uncorrected.

TABLE III

SUBSTITUTED 1,2,3,5-TETRAPHENYL-1,2-DIOLS (COMPOUNDS IV- AND V-)

Starting dione[a]			Products								
								Analyses, %			
								Carbon		Hydrogen	
Code no.	G.	Time, hr.	Diols	M.p., °C.	Yield, G.[b]	%	Empirical formula	Calcd.	Found	Calcd.	Found
II-D	1.0	6	IV-D	213 -213.5	0.29[c,d]	29	$C_{29}H_{24}Cl_2O_2$	73.26	73.15	5.09	4.92
II-E	1.0	6	IV-E	244 -245	.24[c,e]	24	$C_{31}H_{30}O_2$	85.68	85.60	6.96	7.08
II-F	1.5	6	IV-F	201.5-202.5	.27[c,f]	18	$C_{31}H_{30}O_4$	79.80	79.89	6.48	6.75
III-A	1.0	6	V-A	201.5-202.5	.26[c,g]	26	$C_{29}H_{25}ClO_2$	78.99	79.09	5.71	5.56[h]
III-B	1.0	6	V-B	216 -216.5	.11[c,i]	11	$C_{30}H_{28}O_2$	85.68	84.90	6.71	6.80
III-C	1.0[j]	3	V-C	148 -149	.64[k]	64	$C_{30}H_{28}O_3$	82.54	82.14	6.46	6.53
III-D	1.0	6	V-D	220 -221	.34[c,l]	34	$C_{29}H_{25}ClO_2$	78.99	79.08	5.71	5.72[m]
III-J	1.0[j]	3	V-J	148 -149	.64[k]	64	$C_{30}H_{28}O_3$	82.54	82.14	6.46	6.53

[a] For each gram of dione 1 g. of zinc dust and 25–30 ml. of glacial acetic acid were used. Half of this zinc dust was present initially and the remainder was added after half the indicated time had elapsed, except as indicated in footnote *j* below. [b] The analytical sample was prepared by recrystallization from ethanol–benzene to constant melting point, except as indicated in footnote *m* below. [c] Yield is for product obtained after maceration of the tacky crude with warm ethanol or ethanol–benzene prior to recrystallization. No effort was made to recover starting material. [d] M.p. 192–200° after maceration. [e] M.p. 238–240° after maceration. [f] Based on a 0.48-g. aliquot taken from 1.34 g. of total crude diol, m.p. 198.5–201° after maceration. [g] M.p. 197–199° after maceration. [h] *Anal.* Calcd. for $C_{29}H_{25}ClO_2$: Cl, 8.04. Found: Cl, 8.06. [i] M.p. 206–212° after maceration. [j] Ten grams of zinc dust was present initially and none was added at the half-way point. [k] Yield is for product once recrystallized from ethanol. [l] M.p. 213–218° after maceration. [m] *Anal.* Calcd. for $C_{29}H_{25}ClO_2$: Cl, 8.04. Found: Cl, 8.15.

TABLE IV

p-SUBSTITUTED-2,3,4,5-TETRAPHENYLCYCLOPENTADIENES

Starting 1,5-dione		Products								
							Analyses, %			
							Carbon		Hydrogen	
Code no.	G.	Code no.	M.p.,[a] °C.	Yield,[b] G.	%	Empirical formula	Calcd.	Found	Calcd.	Found
II-A	2.00	VI-A	180.5–181.5	0.32	17	$C_{29}H_{20}Cl_2$	79.27	79.10	4.59	4.61[c]
II-B	1.73	VI-B	165.5–166.5	.13	8	$C_{31}H_{26}$	93.42	93.20	6.58	6.64
II-C	1.00	VI-C	221–222	.42	45	$C_{31}H_{26}O_2$	86.48	86.55	6.09	6.15
II-D	2.00	VI-D	190.5–191.5	.054	3	$C_{29}H_{20}Cl_2$	79.27	79.18	4.59	4.39[d]
II-F	0.96	VI-F	146.5–147.5	.044	0.5	$C_{31}H_{26}O_2$	86.48	86.31	6.09	5.95
III-A	2.00	VII-A	141–142	.15	9	$C_{29}H_{21}Cl$	86.01	86.11	5.23	5.37[e]
III-B	2.00	VII-B	162–163	.11	6	$C_{30}H_{24}$	93.71	93.81	6.29	6.07
III-C	1.00	VII-C	130–131	.49	53	$C_{30}H_{24}O$	89.96	89.88	6.04	6.23
III-D	2.95	VII-D	148.5–149.5	.46	17	$C_{29}H_{21}Cl$	86.01	86.26	5.23	5.31[f]
III-E	1.35	VII-E	161–162	.42	34	$C_{30}H_{24}$	93.71	93.68	6.29	6.22
III-J	4.41	VII-J	125.5–126.5[g]	2.32	58	......	...	...	..	..

[a] These are for the analytical samples. [b] Data are for compounds as obtained in Experimental section. [c] *Anal.* Calcd. for $C_{29}H_{20}Cl_2$: Cl, 16.14. Found: Cl, 16.28. [d] *Anal.* Calcd. for $C_{29}H_{20}Cl_2$: Cl, 16.14. Found: Cl, 16.74, 16.51. [e] *Anal.* Calcd. for $C_{29}H_{21}Cl$: Cl, 8.76. Found: Cl, 8.65. [f] *Anal.* Calcd. for $C_{29}H_{21}Cl$: Cl, 8.76. Found: Cl, 8.43. [g] Reported in footnote 11, m.p. 125–126°.

TABLE V

TETRACYCLONES

Starting diene		Products								
							Analyses, %			
							Carbon		Hydrogen	
Code no.	G.	Code no.	M.p., °C.	Yield[a] G.	%	Empirical formula	Calcd.	Found	Calcd.	Found
VI-A	0.050	X-A	252–253[b]	0.029	56[c]	$C_{29}H_{18}Cl_2O$	76.83	76.70	4.00	3.99[d]
VI-B	.030	X-B	222.5–223.0[e]	.012	39[c]	$C_{31}H_{24}O$	90.26	89.79	5.86	6.02
VI-C	.10	X-C	225–226[f]	.063	62[c]	$C_{31}H_{24}O_3$	83.76	83.79	5.44	5.55
VI-D	.025	X-D	238–239[g]	.014	54[h]	$C_{29}H_{18}Cl_2O$	76.83	76.69	4.00	4.00[i]
VI-F	.020	X-F	192–193[j]	.011	54[c]	$C_{31}H_{24}O_3$	83.76	83.75	5.44	5.34
VII-A	.060	XI-A	210.5–211.5[k]	.027	42[h]	$C_{29}H_{19}ClO$	83.14	82.81	4.57	4.63[l]
VII-B	.050	XI-B	224.5–225.0[m]	.031	60[h]	$C_{30}H_{22}O$	90.43	90.34	5.57	5.55
VII-C	.10	XI-C	217–218[n]	.059	57[c]	$C_{30}H_{22}O_2$	86.93	86.62	5.35	5.09
VII-D	.15	XI-D	188–189[o]	.083	52[c]	$C_{29}H_{19}ClO$	83.14	83 51	4.57	4.29[p]
VII-E	.10	XI-E	190.0–191.5[q]	.058	56[h]	$C_{30}H_{22}O$	90.43	90.55	5.57	5.81
VII-J	.50	XI-J	189–190[r]	.31	59[s]	....	...	...	..	...

[a] Yields are based on diene. [b] Reported by F. J. Thaller, D. E. Trucker and E. I. Becker, THIS JOURNAL, **73**, 228 (1951), m.p. 253–254°. [c] Yield is for once chromatographed and once recrystallized product. [d] *Anal.* Calcd. for $C_{29}H_{18}Cl_2O$: Cl, 15.64. Found: Cl, 15.75. [e] Reported[11] m.p. 218–219°. [f] Reported[11] m.p. 222–223°. [g] Reported in footnote *b* above, m.p. 239–240°. [h] Yield is for once chromatographed product. [i] *Anal.* Calcd. for $C_{29}H_{18}Cl_2O$: Cl, 15.64. Found: Cl, 15.56. [j] Reported by S. B. Coan, D. E. Trucker and E. I. Becker, THIS JOURNAL **77**, 60 (1955); m.p. 192.0–192.5°. [k] Reported by S. B. Coan, D. E. Trucker and E. I. Becker, *ibid.*, **76**, 900 (1954), m.p. 211–212°. [l] *Anal.* Calcd. for $C_{29}H_{19}ClO$: Cl, 8.46. Found: Cl, 8.63. [m] Reported in footnote *k*, m.p. 223.8–224°. [n] Reported in footnote *k*, m.p. 217.6–218.0°. [o] Reported in footnote *k*, m.p. 188.3–188.8°. [p] *Anal.* Calcd. for $C_{29}H_{19}ClO$: Cl, 8.46. Found: Cl, 8.69. [q] Reported by footnote *k*, m.p. 190.7–191.1°. [r] Reported: m.p. 189–190°[11] and m.p. 190.0–190.5°, footnote *k*. [s] Yield is for product once recrystallized from benzene:ethanol (1:1).

crops were combined and washed with cold methanol and then with water and finally recrystallized from a minimum volume of glacial acetic acid.

2,4-Bis-(4'-R-phenyl)-1,5-diphenylpentan-1,5-diones (Table I).—The appropriate α-(4-phenyl)-acetophenone was dissolved or suspended in methanol at 45° with mechanical stirring. A solution of potassium hydroxide in 1.5–2.5 ml. of water was added followed by the formalin solution. Stirring was maintained for 1 hr. at this temperature and then the mixture was shaken mechanically for 5–6 hr. at room temperature except where otherwise indicated (Table I). The solid present was filtered and the mother liquor neutralized with acetic acid, concentrated, chilled and filtered again. The second crop was combined with the first only when the melting point of the second was not more than 10° away. The combined crops were washed with cold methanol, then water and finally recrystallized from glacial acetic acid or the designated solvent (Table I).

Unsymmetrically Substituted 1,5-Diones

Methylbenzoin.—The directions of Roger[10] are scanty and so are given here. A solution of methylmagnesium iodide (from 71 g. (0.50 mole)) of methyl iodide and 13.4 g. (0.55 atom) of magnesium was added during 3 hr. with stirring and under nitrogen to a solution of 105 g. (0.50 mole) of benzil in 1250 ml. of ether. After heating for an additional 15 min., a solution of 30 g. of ammonium chloride in 100 ml. of water was added dropwise. The ether later was decanted and the basic magnesium precipitate was washed with ether, combining the washings with the main solutions. After drying the ether solution over anhydrous calcium chloride, filtration and distillation of the ether gave a colorless solid melting at 51–57°. Recrystallization from a mixture of carbon tetrachloride (170 ml.) and petroleum ether (b.p. 60–68°) (100 ml.) and washing the collected solid with petroleum ether (b.p. 28–38°) gave 52 g. of colorless product, m.p. 67–68° (reported m.p. 65–66°,[10] m.p. 68°[14]). Concentration of the mother liquor gave a second crop of 31 g., 64.5–67° (total yield of 83 g., 0.37 mole, 74%).

α-Phenylacrylophenone.—To a solution of 10 g. (0.044 mole) of methylbenzoin in 50 ml. of acetic acid heated to incipient boiling there was added 4 ml. of a 1:1 solution of concentrated sulfuric acid in acetic acid. After from 4 to 5 min. at this temperature with stirring, the solution was poured into 200 ml. of water whereupon a yellow oil separated. The yellow oil was extracted with benzene, the extract dried over anhydrous sodium sulfate and then distilled to give 7.21 g. (0.034 mole, 79%) of yellow α-phenylacrylophenone, b.p. 190° (11 mm.) and 198.5–199° (15 mm.), $n^{25}\mathrm{D}$ 1.6042 (reported[15] b.p. 133–133.8° (<1 mm.), $n^{25}\mathrm{D}$ 1.6028).

The same dimer, m.p. 108–109°, obtained by Burr,[15] was obtained upon letting the product stand for one month at room temperature.

Anal. Calcd. for $(C_{15}H_{12}O)_2$: C, 86.51; H, 5.81. Found: C, 86.38; H, 5.89.

1,3,4-Triphenylpyrazoline.—To a freshly prepared sample of 1.0 g. (5.0 mmoles) of α-phenylacrylophenone dissolved in 10 ml. of ethanol, 0.51 g. (5.0 mmoles) of phenylhydrazine was added. The solution was heated to incipient boiling for 10 min. and then allowed to cool. Filtration and one recrystallization from ethyl acetate afforded 1.18 g. (2.63 mmoles, 79%) of the yellowish-green fluorescing product, m.p. 133.5–135.5°. Two additional recrystallizations gave the analytical sample, m.p. 135–136°.

Anal. Calcd. for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.49; H, 6.02; N, 9.57.

The compound fluoresced blue-white under ultraviolet light.

Unsymmetrically Substituted 1,2,4,5-Tetraphenylpentane-1,5-diones (Table II).—The appropriate α-phenylacetophenone was suspended in the indicated amount of methanol at room temperature and the solution of α-phenylacrylophenone in 5 ml. of methanol was added, and followed by the indicated amount of potassium hydroxide dissolved in a small amount of methanol. The mixture was shaken until all of the solid had gone into solution and allowed to remain at room temperature (25–28°) for the indicated time. It was then chilled and filtered. After washing the collected solid with cold methanol and then water, the product was recrystallized from glacial acetic acid or another solvent (see Table II for other solvents).

3-(4'-Methoxyphenyl)-1,2,5-triphenylpentane-1,5-dione.—A solution of 25 g. (0.105 mole) of 4-methoxychalcone and 20 g. (0.102 mole) of α-phenylacetophenone in 200 ml. of warm methanol was allowed to cool to room temperature. Then 2.95 g. (0.053 mole) of potassium hydroxide dissolved in 6 ml. of methanol was added. The flask was vigorously shaken for 10 min. and the dense, white precipitate that formed was filtered, washed with 50 ml. of methanol and finally with two 100-ml. portions of water and dried. Three recrystallizations from glacial acetic acid afforded 18.6 g. (0.043 mole, 42%) of colorless product, m.p. 149–151° (reported[11] m.p. 154–155°).

4'-Substituted-tetraphenylcyclopentanediols

3-(4'-Chlorophenyl)-1,2,5-triphenylcyclopentane-1,2-diol (V-D).—This example and that in the next paragraph are given to illustrate the general technique followed for the compounds IV and V.

To a solution of 4.0 g. (9.1 mmoles) of III-D dissolved in 100 ml. of warm glacial acetic acid, 20 g. of zinc dust was added. The mixture was refluxed for 5 hr., another 20 g. of zinc dust was added, and the mixture was refluxed an additional 5 hr. After decanting the hot solution from the residual zinc dust into 400 ml. of cold water, the zinc was extracted with 30 ml. of hot acetic acid which was also poured into the cold water. Filtration through a sintered glass funnel gave 3.8 g. of solid, after washing with water and drying. Recrystallization of a 1.0-g. aliquot from benzene: ethanol gave 0.50 g. (1.23 mmoles, 52%) of colorless product, m.p. 217–220°). The analytical sample melted at 220–221°.

4-(4'-Methoxyphenyl)-1,2,3-triphenylcyclopentane-1,2-diol (III-J).—To a solution of 5.0 g. (11.5 mmoles) of 3-(4'-methoxyphenyl)-1,2-triphenylpentan-1,5-dione in 125 ml. of warm acetic acid 25 g. of zinc dust was added. After refluxing for 3 hr. the hot acetic acid solution was decanted into 400 ml. of cold water. The residual zinc was extracted with 50 ml. of hot acetic acid which was decanted into the cold water. Filtration through a sintered glass funnel gave a solid which was taken up in 50 ml. of benzene. The benzene solution was washed with 50 ml. of water, dried over anhydrous sodium sulfate, filtered and concentrated at reduced pressure to give 4.42 g. of crude solid sintering at 144° and melting 149–152°. Recrystallization of 0.50 g. from ethanol gave 0.32 g. (64%) of colorless platelets, m.p. 153–154° (reported[11] m.p. 126–127°). Two additional recrystallizations did not raise the melting point above 153.5–154.5°.

Anal. Calcd. for $C_{30}H_{28}O_3$: C, 82.52; H, 6.46. Found: C, 82.62; H, 6.32.

4'-Substituted-tetraphenylcyclopentadienes

General Procedure.—The procedures of Ziegler and Schnell[5] and of Dilthey, *et al.*,[11] were the models for the syntheses. The diols were isolated as crude materials and subjected to the dehydration step directly without purification. Chromatography on alumina of the reaction mixtures was effected for all reaction mixtures containing dienes, using distilled thiophene-free benzene as solvent and eluant. Many bands were always observed upon chromatography; however, the band containing the desired diene was selected by its blue-white fluorescence under ultraviolet light and by its presence in the lowest or next to the lowest band. All of the dienes were strongly blue-white fluorescent in the solid state or in solution in esters, ketones, alcohols or aliphatic or aromatic hydrocarbons.

2-(4'-Chlorophenyl)-3,4,5-triphenylcyclopentadiene (Table IV, VII-D).—A solution of 2.95 g. (6.73 mmoles) of 2-(4'-chlorophenyl)-1,4,5-triphenylpentane-1,5-dione was converted to 2.5 g. of crude, dry diol (see preceding section) which was dissolved in 60 ml. of warm isobutyl alcohol. Dry hydrogen chloride was passed in for one hour while maintaining the solution at 80–85°. During the first 10 min. needles precipitated. These were filtered (0.42 g.) and shown to be the diol by comparison with that obtained previously. Distillation of the isobutyl alcohol solution almost to dryness and the addition of 20 ml. of methanol gave 0.46 g. (1.14 mmoles, 17%) of pinkish product, m.p. 141–145°.

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(14) C. N. Cameron, *Trans. Roy. Soc. Can.*, **23**, 53 (1929).

(15) J. G. Burr, Jr., THIS JOURNAL, **73**, 5170 (1951).

Recrystallization from 1:1 ethyl acetate–ethanol raised the melting point to 148.5–149.5° and provided VII-D as a light yellow compound. Further recrystallization did not raise the melting point.

2,5-Bis-(4'-chlorophenyl)-3,4-diphenylcyclopentadiene (Table IV, VI-D).—A solution in glacial acetic acid of 2.0 g. (4.22 mmole) of II-D was converted to 1.74 g. of crude, dry diol which was dissolved in 20 ml. of warm isobutyl alcohol. Dry hydrogen chloride was bubbled in and after 0.5 hr. needles precipitated, which were shown to be the diol. Additional isobutyl alcohol was added to effect solution and the addition of dry hydrogen chloride was resumed for an additional 1.5 hr. Removal of the solvent at reduced pressure left a dark brown gum which was taken up in benzene and chromatographed on alumina. The lowest band was pale yellow in visible light, but strongly blue-white fluorescent under ultraviolet light. It was eluted and gave a positive cyclone test (see below). Distillation of the benzene and maceration of the residue with Skellysolve A gave 54 mg. (0.12 mmole, 3%) of pale yellow crystals of VII-D, m.p. 186–189.5°. Recrystallization from ethyl acetate–ethanol raised the melting point to 190.5–191.5°.

2-(4'-Methoxyphenyl)-3,4,5-triphenylcyclopentadiene (Table IV, VII-J).—A solution in acetic acid of 1.00 g. (2.30 mmoles) of III-J was converted to the diol which was extracted with two 75-ml. portions of benzene from the aqueous suspension formed by decanting the hot acetic acid solution of the product into water. The benzene solution was dried over anhydrous sodium sulfate, filtered, evaporated to dryness, and the residue was taken up in 10 ml. of acetic acid and brought to incipient boiling. Four milliliters of a solution of sulfuric acid in acetic acid (1:1 by volume) was added with stirring and the temperature was maintained for three minutes. The solution was poured into 100 ml. of water and extracted with two 50-ml. portions of benzene. After washing the combined extracts twice with water, drying over anhydrous sodium sulfate and filtering, the solution was concentrated to about 4 ml. An equal amount of ethanol was added and on standing at 4° overnight, 0.49 g. (1.22 mmoles, 53%) of almost colorless VII-A was collected (m.p. 128–131°). Chromatography gave a blue-white fluorescing band which was eluted and concentrated to about 3 ml. An equal volume of ethanol was added and, upon cooling, the solution deposited a white solid with a faint yellow tinge, m.p. 130–131°.

Condensation of a portion of this product with *p*-nitrosodimethylaniline gave an anil (IX-J), m.p. 187–188° (see below for details of preparing the anils).

Anal. Calcd. for $C_{38}H_{32}N_2O$: N, 5.26. Found: N, 5.43.

3,4-Bis-(4'-methoxyphenyl)-3,4-diphenylcyclopentadiene (Table IV, VI-C).—As described in the preceding paragraph, 1.0 g. of the dione II-C was converted to the diol, then to the diene, and then the latter was taken up in benzene to give a yellow-brown solution. Concentration of the solution to 4 ml., the addition of 4 ml. of ethanol and cooling afforded 0.42 g. of light tan needles, m.p. 218.5–220°. Two recrystallizations from benzene–ethanol raised the melting point to 221–222°.

An anil (VIII-C) was prepared which melted 223–224.5°, after crystallization from Skellysolve C.

Anal. Calcd. for $C_{39}H_{34}N_2O_2$: C, 83.24; H, 6.09; N, 4.98. Found: C, 83.20; H, 6.40; N, 5.00.

4'-Substituted-tetraphenylcyclopentadienones

The general procedure for the conversion of the dienes (Table IV) to their corresponding cyclones (Table V) was effected over their dimethylaminoanils and was patterned after the procedures of Ziegler and Schnell[5] for the conversion of tetraphenylcyclopentadiene to tetracyclone. The crude dimethylaminoanils were not isolated, but were directly hydrolyzed to the cyclones.

The indicated amount of diene (Table V) was dissolved in 4–5 ml. of benzene–methanol (3:1 or 4:1) to which was added approximately three times the molar quantity of *p*-nitrosodimethylaniline. At incipient boiling, from 3–5 drops of 10% sodium methoxide in methanol was added and the temperature was maintained at just below reflux for from 5–10 min. Concentrated hydrochloric acid (5–10 ml.) was added and the mixture was boiled for from 10–15 min. Extraction of the cooled mixture with 10 ml. of benzene was followed by washing the benzene layer with water, drying it over anhydrous sodium sulfate, filtering it and distilling the solvent. The residual solid was taken up in benzene and chromatographed and developed with benzene. The red-violet band was eluted and distilled to dryness. A melting point was taken and a mixture melting point with the conventionally prepared cyclone.[16,17] The analytical samples were prepared by recrystallization from minimum quantities of benzene. Alternatively, the benzene solution was concentrated to 1 ml., 1 ml. of ethanol was added and the solution was chilled and filtered.

Melting points were taken on about 0.5-mg. quantities using thin wall capillary tubes. A typical synthesis follows.

2-(4'-Tolyl)-3,4,5-triphenylcyclopentadienone.—A solution was prepared of 0.10 g. (0.260 mmole) of 2-(4'-tolyl)-3,4,5-triphenylcyclopentadiene and 0.12 g. (0.80 mmole) of *p*-nitrosodimethylaniline in (3:1) warm benzene–methanol (4 ml.). The solution was brought to incipient reflux and five drops of sodium ethoxide (10%) was added, whereupon the solution immediately turned a deep brown. Heating at incipient reflux was continued for ten minutes and the flask was allowed to cool, at which time hydrochloric acid (10 ml.) was added to hydrolyze the dimethylaminoanil. Heating at incipient reflux was maintained for an additional ten minutes. The flask was cooled, and benzene (10 ml.) was added and the aqueous phase discarded. The organic layer was washed with two 20-ml. portions of water and dried over anhydrous sodium sulfate, filtered and distilled to dryness to remove all traces of alcohol. The dark brown-violet residue was redissolved in approximately 5 ml. of benzene and chromatographed on alumina (F-20). The chromatogram was developed with benzene and the red-violet band (lowest colored band) was eluted with the same solvent. The percolate was distilled to dryness leaving a purplish-red solid, m.p. 188–189°. The solid was dissolved in a minimum amount of hot benzene–ethanol (1:1) and recrystallized. The dark crystals were filtered to give 58 mg. (0.145 mmole, 56%) of product, m.p. 190–190.5° (reported 190.7–191.1°[16]).

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(16) S. B. Coan, D. E. Trucker and E. I. Becker, THIS JOURNAL, **75**, 900 (1953).

(17) S. B. Coan, D. E. Trucker and E. I. Becker, *ibid.*, **77**, 60 (1955).