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

The Synthesis of Some Alkoxy- and Alkyl-substituted Tetraphenylcyclopentadienones

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The syntheses for the homologous series of ethers (alkoxytetracyclones) from C_1 to C_{11} of 2,4,5-triphenyl-3-(4′-hydroxyphenyl)cyclopentadienone are described. A number of related alkyltetraphenylcyclopentadienones are also described.

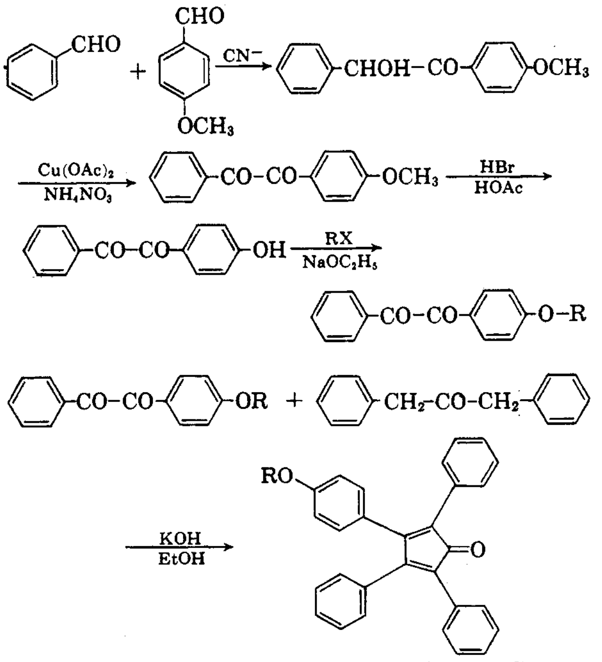
The fact that 2,4,5-triphenyl-3-(4′-octoxyphenyl)cyclopentadienone melts at 96.5–98.0° while tetracyclone (tetraphenylcyclopentadienone) melts at 219–220°[3] prompted a study of the melting point behavior of the compounds in between.

The substituted tetraphenylcyclopentadienones were arrived at by two different synthetic routes.

(1) Benzanisoin prepared by a mixed benzoin reaction between benzaldehyde and *p*-anisaldehyde was oxidized and the resulting *p*-methoxybenzil was demethylated to *p*-hydroxybenzil by means of hydrobromic acid in acetic acid. Alkylation of the hydroxybenzil with different alkyl halides gave a series of *n*-alkoxybenzils, which were condensed with benzyl ketone to give the corresponding 2,4,5-triphenyl-3-(4′-*n*-alkoxyphenyl)cyclopentadienones.

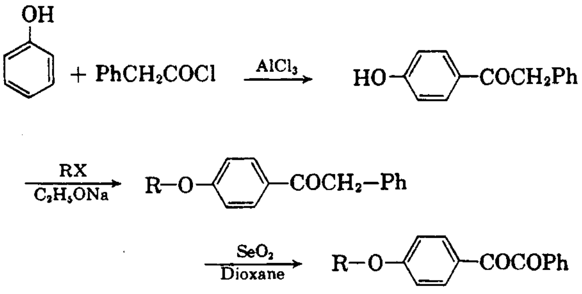
CHART I

ALKOXYTETRAPHENYLCYCLOPENTADIENONES



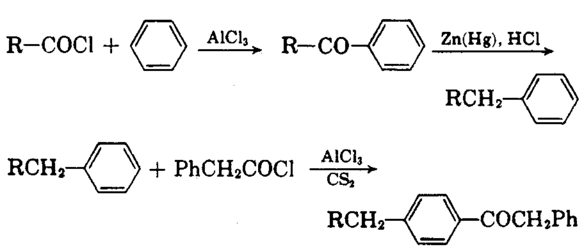
R = C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}, n-C_8H_{17}, n-C_9H_{19}, n-$C_{10}H_{21}$ and n-$C_{11}H_{23}$

(2) A second route to the alkoxybenzils was *via* 4-hydroxy-α-phenylacetophenone, which was first prepared by the acylation of phenol. Alkylation gave the alkoxy-α-phenylacetophenones which were then oxidized to the corresponding benzils with selenium dioxide. This route required chromatographic purification of the benzil; the route through hydroxybenzil was preferred.



R = n-C_3H_7 and iso-C_3H_7

The 4-*n*-butyl, and 4-isobutyl-α-phenylacetophenones were prepared by the following route:



The 4-neopentyl-α-phenylacetophenone required special consideration. The literature describes the preparation of neopentylbenzene from benzylmagnesium chloride and *tert*-butyl chloride.[4,5] It was thought desirable to prepare it here by the reduction of pivalophenone. Therefore, isobutyrophenone, which had been prepared as above, was alkylated with methyl iodide and sodamide.[6] Reduction of the carbonyl group to the methylene group was carried out both by the Clemmensen[7]

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[1] Taken from the M.S. theses of A.F. (1953) and W.G. (1956), and from a portion of the Ph.D. dissertation of L.M. (1953).

[2] To whom inquiries should be sent.

[3] L. Mehr, Ph.D. dissertation, Polytechnic Institute of Brooklyn (1953).

[4] E. Berliner and F. Berliner, *J. Am. Chem. Soc.*, **71**, 1195 (1949).

[5] A. Bygdén, *Ber.*, **45**, 3479 (1912).

[6] A. Haller and E. Bauer. *Compt. rend.*, **148**, 70 (1909).

[7] E. Clemmensen, *Ber.*, **46**, 1837 (1913).

reduction and Huang-Minlon modification[8] of the Wolff-Kishner reduction. Mixture melting points of the 4-alkyl-α-phenylacetophenones prepared from each of the reduction products showed no depression. This precaution ruled out the possibility that rearrangement had taken place during the Clemmensen reduction, although this conclusion was based on the reasonable, but unproved assumption that the base-catalyzed reduction would proceed without rearrangement.

The alkyl and alkoxy substituted tetraphenylcyclopentadienones were prepared by the method of Dilthey and Quint[9] as modified by Johnson and Grummitt.[10] The products obtained by cooling the reaction mixture varied from solids, which could be purified by crystallization alone, to semi-solid colored oils which required chromatography in addition. It should be noted that the 2,4,5-triphenyl-3-(4′-neopentylphenyl)cyclopentadienone was isolated in two different crystalline modifications melting at 153.5–154.0° and at 169–170°. A mixture of the two melted at 169–170°.

TABLE I

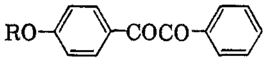
MELTING POINTS OF 2,4,5-TRIPHENYL-3-(4′-*n*-ALKOXYPHENYL)CYCLOPENTADIENONES

R	M.P., °C.
CH_3O	213–214[a]
C_2H_5O	171–172
n-C_3H_7O	182.5–183.5
n-C_4H_9O	144.5–145.5
n-$C_5H_{11}O$	184.3–185.1
n-$C_6H_{13}O$	140.8–141.5
n-$C_7H_{15}O$	142.1–143.0
n-$C_8H_{17}O$	96.5–98.0
n-$C_9H_{19}O$	115.3–115.7
n-$C_{10}H_{21}O$	134.0–134.7
n-$C_{11}H_{23}O$	125.0–125.6

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

TABLE II

MELTING POINTS OF 4-*n*-ALKOXYBENZILS



R	M.P., °C.
CH_3	61.5–63.0[a]
C_2H_5	69.5–70.5[a]
C_3H_7	102.5–103.5[b]
C_4H_9	59.5–60.0[c]
C_5H_{11}	37–38[a]
C_6H_{13}	51.5–52.5[a]
C_7H_{15}	55–56[a]
C_8H_{17}	37–38[a]
C_9H_{19}	32.3–33.0
$C_{10}H_{21}$	37–38[a]
$C_{11}H_{23}$	42.0–43

[a] Footnote 25. [b] Footnote 25 reported 102–103°. [c] Footnote 25 reported 58–59°.

The variations of the melting points of the alkoxytetracyclones and of the alkoxybenzils are noteworthy. The alkoxytetracyclones show a typical alternation, with the melting point of the alkoxytetracyclone having an odd number of carbon atoms lying above those of its homologs, except for ten carbon atoms. Such changes have been associated previously with a change in crystal structure, but the necessary single crystal data were not obtained here. Among the benzils the alternation of melting points is not observed. No explanation for this is offered.

EXPERIMENTAL

4-Hydroxybenzil. 4-Methoxybenzil (50 g., 0.208 mole) was dissolved in a mixture of 500 ml. of 48% hydrobromic acid and 250 ml. of glacial acetic acid. The mixture was refluxed for 4 hr. at which time it became homogeneous. After cooling, the reaction mixture was poured with stirring into 1 l. of cold water. The pale yellow solid which formed was filtered, washed with water, dried, and then dissolved in 200 ml. of ethyl ether. This solution was extracted with 250 ml. of 10% potassium hydroxide solution, and divided into four equal portions. The ether layer, after being dried over anhydrous sodium sulfate, was evaporated to dryness, and the residue was recrystallized from absolute ethanol to give 8 g. (0.033 mole) of unreacted 4-methoxybenzil. The aqueous phase was acidified with 1:1 hydrochloric acid and yielded, after filtration, 37.2 g. (0.165 mole, 94%) of product based on 4-methoxybenzil not recovered, m.p. 127–129° (lit.[11] m.p. 129–130°).

The purification of a number of the alkyl bromides was carried out by a modification of a procedure described by Vogel.[12]

Alkyl bromides. The commercial alkyl bromide was dissolved in previously purified petroleum ether (b.p. 68–69°) to give a 1.0:2.5 mixture. This mixture was washed successively with concentrated sulfuric acid, water, 10% sodium hydroxide, and again with water. After being dried over anhydrous sodium sulfate, the mixture was distilled to give the desired alkyl bromide. The boiling point, density, index of refraction, molar refraction, and in some cases the melting point were used as a criteria of purity.

4-Hydroxy-α-phenylacetophenone. Phenol (12.2 g., 0.13 mole) and phenylacetyl chloride (20 g., 0.13 mole) were added to 115 ml of nitrobenzene and heated for 1 hr. at 80–85°. Then aluminum chloride (22.7 g., 0.17 mole) was added slowly and the reaction mixture was kept at 80° for 1 hr. The mixture, after cooling to room temperature, was poured into 300 g. of acidified ice water and extracted with 400 ml. of ether. The ether layer was washed twice with 300 ml. of water and then extracted twice with 100 ml. portions of 10% sodium hydroxide solution. The basic solution was neutralized with hydrochloric acid, cooled, and the brown precipitate collected. This was purified by chromatographing it on an alumina column from a minimum amount of methanol. Precipitation with water and filtration gave 13 g. (0.0613 mole, 47.3%) of a white powder, m.p. 148–149° (lit. m.p. 142°,[13] 146–147°[14]).

4-Alkyl-α-phenylacetophenones. The intermediate alkylbenzenes were prepared by the Friedel and Crafts acylation

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(8) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(9) W. Dilthey and F. Quint, *J. prakt. Chem.*, (2) **128**, 139 (1930).

(10) J. R. Johnson and O. Grummit, *Org. Syntheses*, **Coll. Vol. III**, 806 (1955).

(11) J. H. Gorvin, *Nature*, **161**, 208 (1948).

(12) A. I. Vogel, *J. Chem. Soc.*, 636, 647 (1943).

(13) S. Weisl, *Monatsh*, **26**, 977 (1905).

(14) W. Dilthey and W. Schneider-Windmüller, *J. prakt. Chem.*, **159**, 273 (1943).

TABLE III

n-ALKYL BROMIDES, R—BR

R	B.P., °C. (mm. of Hg)	1 Atm.[a]	d_4^{20}	n_D^{20}	R_n Calcd.	R_n Obsd.
C_5H_{11}	33 (19)	131[b]	1.2197[c]	1.4550[d]	33.04	32.96
C_6H_{13}	56 (22)	157[e]	1.1694[f]	1.4470[g]	37.69	37.74
C_7H_{15}	49 (6)	180[h]	1.1398[i]	1.4500[j]	42.29	42.23
C_9H_{19}	69 (35)	221[k]	1.0853[l,m]	1.4524[l,n]	51.53	51.50
$C_{10}H_{21}$[o]	65 (1)	245[p]	1.0714[q]	1.4560[r]	56.15	56.12
$C_{11}H_{23}$[s]	64–71 (1)		1.0550[t]	1.4570[u]	60.76	60.72

[a] Boiling points at 1 atmosphere calculated from R. R. Driesbach, *Pressure-Volume-Temperature Relationships of Organic Compounds*, Handbook Publishers, Inc., Sandusky, Ohio, 1952. [b] N. A. Lange, *Handbook of Chemistry*, 7th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949, reported 129.7°. [c] Ref. 12 reported 1.2190. [d] Ref. 12 reported 1.44505. [e] *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., 35th ed., 1953, reported 156.0°. [f] Ref. 12 reported 1.1705. [g] Ref. 12 reported 1.44781. [h] J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier Publishing Co., 1950, reported 180.0°. [i] Footnote *h* reported 1.1398. [j] Ref. 12 reported 1.45052. [k] Ref. 12 reported 219° (745.5 mm.). [l] Value determined at 25°. [m] L. M. Ellis, Jr., and E. E. Reid [*J. Am. Chem. Soc.*, **54**, 1674 (1932)] reported 1.08490. [n] Footnote *m* reported 1.4523. [o] (1) M.p. −28° to −27°, J. D. Meyer and E. E. Reid [*J. Am. Chem. Soc.*, **55**, 1574 (1933)] reported −29.62°; (2) T. Kaneko and T. Amazaki [*Nippon Kagaku Zasshi*, **76**, 281 (1955); *Chem. Abstr.*, **51**, 17722a (1957)] report m.p. −30°. [p] Footnote 12 reported 102.5° (5.9 mm.). B.p. at 1 atm. calculated according to footnote *a* is 250°. [q] Footnote 12 reported 1.0658. [r] Footnote 12 reported 1.45527. [s] M.p. −24° to −23°. Footnote *o* (1) reported −13.15° and footnote *o* (2) reported m.p. −9°. [t] Footnote 12 reported 1.0541. [u] Footnote 12 reported 1.45697.

of benzene followed by the reduction of the resulting alkylaryl ketone as described below.

Pivalophenone. Isopropyl phenyl ketone (50 g., 0.337 mole) was methylated with methyl iodide and sodamide according to the method of Haller and Bauer[6] giving 47 g. (0.29 mole, 86%) of pivalophenone, b.p. 93.8–94.3° (8.5–9.0 mm.), n_D^{20} 1.5080 [lit.[15] b.p. 80–84° (3 mm.), n_D^{20} 1.5102]. The semicarbazone melted at 158–159° (lit.[16] 159°); the oxime melted at 165–166° (lit.[15] m.p. 194–195°).

Alkylbenzenes. The three ketones were reduced by the method of Clemmensen.[6] Pivalophenone was also reduced by the Huang-Minlon modification[8] of the Wolff-Kischner reaction. *n*-Butylbenzene, b.p. 180–182° (760 mm.), n_D^{20} 1.4929 [lit. b.p. 180–185° (760 mm.);[7] n_D^{20} 1.4899,[17] 1.4936[18]]. Isobutylbenzene, b.p. 170–173° (760 mm.), n_D^{20} 1.4920 [lit. b.p. 169.0–169.5° (760 mm.),[19] n_D^{20} 1.4871,[20] $n_D^{18.5}$ 1.4934[21]].

In the preparation of neopentylbenzene, zinc amalgam, made from 100 g. of mossy zinc, was covered with 50 ml. of water and 50 ml. of concentrated hydrochloric acid and then pivalophenone (10.1 g., 0.0623 mole) was added and the mixture was refluxed vigorously for 24 hr. For the first 10 hr. 20 ml. of concentrated hydrochloric acid was added each hour (10 additions). At the end of 10 hr. fresh zinc amalgam made from 125 g. of mossy zinc was added with 50 ml. of concentrated hydrochloric acid and the mixture was refluxed for the remaining 14 hr. At the end of the reaction the mixture was extracted with 150 ml. of ether and the two phases separated. The ether layer was washed twice with 100 ml. of water, dried over anhydrous magnesium sulfate and then the ether was removed on a water bath. The reaction gave 5.6 g. (0.0377 mole, 60.7%) of neopentylbenzene, b.p. 68–70° (12 mm.), n_D^{20} 1.4950.

The same substance was also prepared by the Huang-Minlon[8] modification of the Wolff-Kishner reduction. Pivalophenone (10 g., 0.0616 mole), triethylene glycol (65 ml.), potassium hydroxide (9.6 g.) and 85% hydrazine hydrate (6.5 ml.) were mixed and refluxed for 1.5 hr. Water was removed by means of a Dean-Stark trap until the temperature was brought up to 190°. After 3 hr. at this temperature, the reaction mixture was cooled to room temperature, combined with the aqueous distillate, and extracted with two 50-ml. portions of ether. The ether solution was washed with 100 ml. of water, dried over anhydrous magnesium sulfate, after which the solvent was removed on a water bath. Fractional distillation of the residue gave 5.8 g. (0.0391 mole), 63.4% of neopentylbenzene, b.p. 78–80° (21 mm.), n_D^{20} 1.4865 [lit. b.p. 185–186° (760 mm.)[22] n_D^{20} 1.4870,[4] 1.4885[22]].

4-Alkyl-α-phenylacetophenones. The three 4-alkyl-α-phenylacetophenones were made by similar procedures. The quantities given are for making 4-*n*-butyl-α-phenylacetophenone; the others used the same ratios of starting materials.

Aluminum chloride (12.9 g., 0.0969 mole) and phenylacetyl chloride (11.5 g., 0.0745 mole) were added to 100 ml. of carbon bisulfide. The alkylbenzene (0.0745 mole) was added dropwise to the reaction mixture. The mixture was refluxed for 15–20 min., cooled to room temperature, and poured into acidified ice water, which was extracted with 400 ml. of ether. The two phases were separated and the ether layer was washed twice with 400 ml. of water, once with 100 ml. of 5% sodium hydroxide solution and again with 400 ml. of water. After drying the ether solution over anhydrous magnesium sulfate, it was distilled to dryness. The residue was chromatographed in benzene solution on an alumina column. The eluant was concentrated, clarified with charcoal, and then evaporated to dryness. Crystallization of the residue from methanol gave the product. Isobutylbenzene (20 g., 0.149 mole) gave 24.5 g. (0.097 mole, 65.3%) of 4-isobutyl-α-phenylacetophenone, m.p. 52.5–53.5°. *n*-Butylbenzene (10 g., 0.0745 mole) gave 14.5 g. (0.0573 mole, 77.3%) of 4-*n*-butyl-α-phenylacetophenone, m.p. 63.5–64.0°. Neopentylbenzene (5.6 g., 0.0378 mole) gave 7.8 g. (0.0292 mole, 78%) of 4-neopentyl-α-phenylacetophenone, m.p. 80–81°.

Benzils. A mixture of 4-alkoxy-α-phenylacetophenone and selenium dioxide in acetic anhydride was heated at 144–145° in an oil bath for 4 hr. The reaction mixture was cooled and the selenium which precipitated was filtered and washed with 2–3 ml. of acetic anhydride, which was added to the filtrate. After warming the solution with 150 ml. of water, the benzil was extracted with ether. The ether layer was separated, washed once with an equal volume of water, and dried over anhydrous calcium chloride. The solvent was removed by distillation and in some cases the benzil was obtained by distilling it at reduced pressure. Some selenium remained in the product which was removed by chromatography from ethanol on an alumina column. The product was then crystallized to constant melting point from ethanol (see Table IV).

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(15) J. H. Ford, C. D. Thompson, and C. S. Marvel, *J. Am. Chem. Soc.*, **57**, 2619 (1935).

(16) P. Lucas, *Compt. rend.*, **152**, 1771 (1911).

(17) A. W. Schmidt, G. Hopp, and V. Schoeller, *Ber.*, **72**, 1893 (1939).

(18) J. v. Braun and H. Deutsch, *Ber.*, **45**, 2171 (1912).

(19) W. H. Perkin, *J. Chem. Soc.*, **77**, 267 (1900).

(20) G. F. Hennion and L. A. Auspos, *J. Am. Chem. Soc.*, **65**, 1603 (1943).

(21) E. Boedtker, *Bull. soc. chim.*, [3] **31**, 965 (1904).

(22) V. N. Ipatieff and L. Schmerling, *J. Am. Chem. Soc.*, **60**, 1476 (1938).

TABLE IV

4-ALKOXYBENZILS *via* OXIDATION OF 4-ALKOXY-α-PHENYLACETOPHENONES WITH SELENIUM DIOXIDE IN ACETIC ANHYDRIDE

	Starting Materials					Product		
	Acetophenone		Selenium Dioxide		Acetic Anhydride,			Yield,
R	Grams	Mmole	Grams	Mmole	Ml.	M.P., °C.	Grams	%
C_2H_5	5.0	20.8	2.54	22.9	7.0	68–69[a]	4.1	78
n-C_4H_9	6.0	22.4	2.72	24.6	10.0	59.5[b]–60.0[c]	4.3	68
n-C_8H_{17}	9.0	27.7	3.38	30.5	18.0	37[d]–38[e]	6.2	66

[a] Footnote 23 reported 69.5–70.5°. [b] Footnote 23 reported 58–59° in 52% yield. [c] B.p. 204 (4 mm.). [d] Footnote 23 reported 37–38° in 5% yield. [e] B.p. 247–248° (3 mm.).

TABLE V

SUBSTITUTED BENZILS *via* OXIDATION OF 4-SUBSTITUTED-α-PHENYLACETOPHENONES WITH SELENIUM DIOXIDE IN DIOXANE

	Starting Materials				Products						
	4-Substituted-α-phenylaceto-phenones		Selenium dioxide (mole) / Acetophenone (mole)	Dioxane (mole) / Acetophenone (mole)				Analyses			
								Carbon		Hydrogen	
Y	Grams	Mole			M.P., °C.	Yield, %	Empirical formula	Calcd.	Found	Calcd.	Found
n-C_3H_7O	20	0.079	1.1	5.7	102.5–103.5[a]	81.5					
iso-C_3H_7O	20	0.079	1.1	5.7	30–31[b,c]	76.5					
n-C_4H_9	12	0.0476	1.1	5.7	Liq[d]	95	$C_{18}H_{18}O_2$	81.17	81.09	6.81	6.90
iso-C_4H_9	12	0.0476	1.1	5.7	Liq[e]	96.3	$C_{18}H_{18}O_2$	81.17	81.43	6.81	6.96
neo-C_5H_{11}	12.8	0.048	1.1	5.7	52–53[f]	86	$C_{19}H_{20}O_2$	81.40	81.41	7.19	7.28

[a] Footnote 23 reported 102–103°. [b] Footnote 23 reported 30–31°. [c] Yield reported as liquid, b.p. 219–220° (6 mm.). [d] B.p. 147–148° (0.1 mm.), n_D^{25} 1.5773. [e] B.p. 168–169° (1 mm.), n_D^{25} 1.5762. [f] B.p. 192–194° (0.5 mm.).

TABLE VI

SYNTHESIS OF 4-ALKOXYBENZILS *via* ALKYLATION OF 4-HYDROXYBENZIL

Starting Materials[a]		Products						
					Analyses			
					Carbon		Hydrogen	
R	Alkyl bromide, *G*	Empirical formula	M.P., °C.	Yield,[c] %	Calcd.	Found	Calcd.	Found
C_2H_5	20.67[b]		68.5–70.0[d]	92				
n-C_3H_7	16.36		101.5–103.0[e]	89				
n-C_4H_9	18.08		58.0–59.5[f]	75				
n-C_5H_{11}	20.1		35.5–36.7[g]	58				
n-C_6H_{13}	21.9		50.0–51.8[h]	69				
n-C_7H_{15}	23.8		53.2–55.4[i]	78.5				
n-C_8H_{17}	25.7		36.0–38.0[j]	88				
n-C_9H_{19}	27.5	$C_{23}H_{28}O_3$	32.3–33.0	72	78.37	77.96	8.01	7.85
n-$C_{10}H_{21}$	29.4	$C_{24}H_{30}O_3$	34.7–35.4[k]	68	78.65	78.56	8.25	8.25
n-$C_{11}H_{23}$	31.3	$C_{25}H_{32}O_8$	42.0–43.0	33	78.91	78.94	8.48	8.54

[a] Alkyl bromide (0.133 mole), 4-hydroxybenzil (10.0 g., 0.0442 mole), sodium (1.02 g., 0.0442 atom), and 125 ml. of ethanol. [b] The iodide was used. [c] All yields based on 4-hydroxybenzil. [d] Footnote 23 reported 69.5–70.0°. [e] Footnote 23 reported 102.0–103.0°. [f] Footnote 23 reported 58.0–59.0°. [g] Footnote 23 reported 37–38°. [h] Footnote 23 reported 51.5–52.5°. [i] Footnote 23 reported 55–56°. [j] Footnote 23 reported 37.0–38.0°. [k] Footnote 23 reported 36–37°. There is a printing error in the empirical formula for the benzil, but our constants agree.

The remaining benzils were prepared according to Bockstahler and Wright[23] and are listed in Table V.

4-Alkyl or alkoxy-α-phenylacetophenone (0.0476 mole), dioxane 24 g., (0.272 mole), selenium dioxide (5.88 g., 0.053 mole) and water (0.054 g., 0.053 mole) were mixed and refluxed for 6–8 hr. The hot mixture was suction filtered and the selenium residue washed with 15–25 ml. of hot dioxane. The dioxane was removed by distillation under vacuum and the benzil purified by distillation, chromatography, and crystallization as needed.

4-Alkoxybenzils. 4-Hydroxybenzil (10 g., 0.0442 mole) and alkyl bromide (0.133 mole) were added to a mixture of metallic sodium (1.02 g., 0.0442 atom) in 125 ml. of absolute ethanol and refluxed until the dark brown solution formed by the hydroxybenzil and sodium ethoxide turned pale yellow.

The reaction mixture was then cooled in a Dry Ice chest and filtered with suction at about −75°. The precipitate

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(23) E. R. Bockstahler and D. L. Wright, *J. Am. Chem. Soc.*, **71**, 3760 (1949).

TABLE VII

SUBSTITUTED TETRAPHENYLCYCLOPENTADIENONES

Benzil[a]		Products						
					Analyses			
					Carbon		Hydrogen	
Y	Grams	Yield, %	M.P., °C.	Empirical formula	Calcd.	Found	Calcd.	Found
						89.89		5.95
n-C_4H_9	6.0	21.8	122.0–122.5	$C_{33}H_{28}O$	89.96	89.76	6.41	6.35
						89.90		6.41
iso-C_4H_9	6.0	27.6	132.5–133.0	$C_{33}H_{28}O$	89.96	90.12	6.41	6.59
						90.22		6.58
neo-C_5H_{11}	6.3	12.7	153.5–154.0[b]	$C_{34}H_{30}O$	89.83	89.80	6.65	6.77
		16.6	169–170[b]	$C_{34}H_{30}O$				
C_2H_5O	1.22	69	171–172	$C_{31}H_{24}O_2$	86.89	86.65	5.65	5.44
n-C_3H_7O	7.0	64.5	182.5–183.5	$C_{32}H_{26}O_2$	86.85	87.28	5.92	6.10
						87.06		5.99
iso-C_3H_7O	7.0	60	176–177	$C_{32}H_{26}O_2$	86.85	87.25	5.92	6.01
n-C_4H_9O	1.2	66	144.5–145.5	$C_{33}H_{28}O_2$	86.81	86.61	6.18	6.27
n-$C_5H_{11}O$	4.26	63.8	184.3–185.1	$C_{34}H_{30}O_2$	86.77	86.82	6.43	6.69
n-$C_6H_{13}O$	4.46	50.2	140.8–141.5	$C_{35}H_{32}O_2$	86.74	86.79	6.66	6.67
n-$C_7H_{15}O$	4.67	29.0	142.1–143.0	$C_{36}H_{34}O_2$	86.71	86.37	6.87	6.97
n-$C_8H_{17}O$	2.0	63	96.5–98.0	$C_{37}H_{36}O_2$	86.68	86.46	7.08	6.94
n-$C_9H_{19}O$	5.07	28.7	115.3–115.7	$C_{38}H_{38}O_2$	86.65	86.55	7.27	7.20
n-$C_{10}H_{21}O$	5.27	40.7	134.0–134.7	$C_{39}H_{40}O_2$	86.62	86.74	7.46	7.58
n-$C_{11}H_{23}O$	2.73	30.1	125.0–126.6	$C_{40}H_{42}O_2$	86.60	86.40	7.63	7.53

[a] An equivalent number of moles of benzyl ketone were employed. [b] Mixture melting point 169–170° with the compound immediately above.

was washed with cold water, dried in a desiccator, and then recrystallized from absolute ethanol.

2,3,4,5-Tetraphenylcyclopentadienones.[9,10] Alkyl or alkoxybenzil and an equivalent quantity of benzyl ketone in 15–25 ml. of absolute ethanol (purified by distillation from either potassium hydroxide or sodium ethoxide) was heated to boiling and a solution of potassium hydroxide in 1–2 ml. of ethanol was added and the mixture was refluxed for 15 min. The crude product was isolated by cooling the reaction mixture in a salt-ice bath. The precipitate which formed was filtered, washed with cold ethanol, and then purified by chromatography from benzene on alumina. The percolates were evaporated to dryness and the residue recrystallized from a benzene-ethanol mixture.

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Effect of Substitution in the Aniline Portion on the Behavior of Semianilides of β-Arylglutaconic Acids

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Semianilides of β-arylglutaconic acids are ordinarily found to exist in the cis form, but if the aniline portion of the semianilide is made to carry a carbomethoxy substituent in the ortho position, then the resulting *o*-carbomethoxysemianilides can be obtained as well-defined cis and trans modifications. The cis *o*-carbomethoxysemianilides are found to lose one molecule of water in two different ways, under different conditions, yielding (a) a lactonic substance and (b) the corresponding hydroxy anil.

The chemistry of substituted and unsubstituted glutaconic acids has been previously studied, principally by Thorpe *et al.*[2,3] and by other workers.[4–6] By analogy with the existence of well defined cis and trans modifications of maleic and fumaric acids, Thorpe postulated that glutaconic acids should exist in three forms namely, cis, trans, and labile.[3] The labile form was, however, found to be nonexistent. Also, attempts to isolate the simple unsubstituted glutaconic acids in cis and trans modifications failed, although Perkin *et al.*[5] were able to obtain some alkyl substituted glutaconic

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