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Fulvenes and Thermochromic Ethylenes. Part 30.* Experiments in the 2,3-Diarylindone Series

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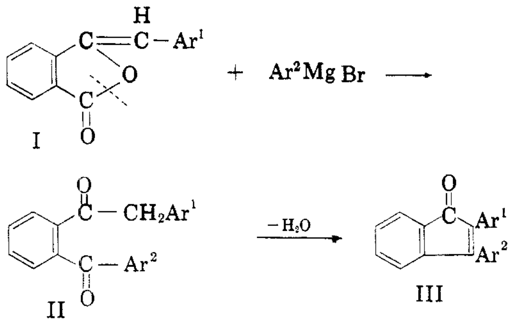
By the reaction of arylmethylene-phthalides (I) with aromatic Grignard compounds, twelve 2,3-diarylindones, nine of them new compounds, have been prepared. In three cases, compounds of the type II have been isolated as intermediary products of the synthesis. The infrared, ultraviolet, and visible spectra of the diaryl-indones have been measured. It is not possible to assign the two longest absorption bands of the diarylindones to specific "absorption paths," as it has been done in the case of the analogously built tetraarylcyclopentadienones.

The synthesis of 2,3-diarylindones (III) from arylmethylenephthalides (I) and aromatic Grignard compounds[1-4] has been formulated as follows: The Grignard compound opens the heterocyclic ring[5-10] (along the dotted line) in I; the enol formed (after hydrolysis) isomerizes to the *o*-arylacetylbenzophenone (II) and the latter loses water to yield III. The last reaction often can be observed qualitatively, when the reaction product is worked up with acid; a sudden change in color takes place, indicating the formation of the 2,3-diarylindone (III).

During a study of the properties of 2,3-diarylindones, intermediates of type II have been isolated in a number of cases; it has been shown that their transformation into III can be effected by heating to temperatures of about 180°.



The arylmethylenephthalides (I) are obtained by the condensation of phthalic anhydride with arylacetic acids in the presence of sodium acetate as catalyst;[11] their absorption spectra and some other properties are listed in Table I.

The spectrum of benzylidenephthalide should resemble that of stilbene[15] (main maximum 2970 Å; less pronounced maximum 3140 Å), but be shifted towards the visible under the influence of the auxochromic enol ester system present. This expectation is borne out by the experiment. Also, the influence of substituents in the arylmethylene group on the absorption is normal. While it appears impossible to decide whether the configuration of the compounds is *cis*- or *trans*, it is reasonable to deduce from the experimental data that all compounds described have the same configuration, with the exception of β-naphthylmethylenephthalide which absorbs at a much lower wave length than the corresponding α-compound, whilst the reverse should be true if the two substances had the same configuration (larger steric hindrance in the α-naphthyl compound). If the β-naphthyl compound is, then, assumed to have the *cis*-configuration, all the other derivatives would be the *trans*-forms.

In three cases, colorless intermediates (II) have been isolated from the reaction of arylmethylenephthalides (I) with aromatic Grignard compounds; as already pointed out, they are converted into the corresponding 2,3-diarylindones (III) by heating. An analogous reaction has been observed in the transformation of 2-benzoyl-ω-bromoacetophenone to 2-bromo-3-phenyl-indone by A. F. Harms and W. Th. Nauta.[16] For the case of the product from β-naphthylmethylenephthalide and phenylmagnesium bromide, formula (II, Ar^1 = β-naphthyl, Ar^2 = phenyl) is supported by the infrared spec-

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(12) *Cf.* D. S. Pratt, *Phillippine J. Science*, **8a**, 309 (1914) (*Chem. Centralbl.*, **II**, 473 (1914)).

(13) C. F. H. Allen and J. W. Gates [*J. Am. Chem. Soc.*, **65**, 419 (1943)] give m.p. 154–155°.

(14) O. Blank [*Ber.*, **29**, 2373 (1896)] gives m.p. 170–171°.

(15) K. W. Hausser, R. Kuhn, and A. Smakula, *Ztschr. physikal. Chem.*, **B**, **29**, 384 (1935); E. A. Braude, *J. Chem. Soc.*, 1902 (1949).

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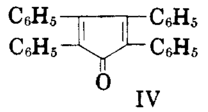
trum; the band at 1686 cm^{-1} corresponds to that expected for an alkyl aryl ketone.[17] The band characteristic of the diaryl ketone grouping (at 1663 cm^{-1}) has not been found; it may have been obscured by the strong 1686 cm^{-1} band, or its frequency may have been raised by the neighboring second carbonyl group.

The properties of the 2,3-diarylindones (III) prepared, including their absorption spectra, are summarized in Table II. A preliminary communication on some of the spectra has been published elsewhere.[18]

The spectra showed two main bands, which, in the case of the parent substance (I, $Ar^1 = Ar^2 =$ phenyl), lie at 2560 and 4400 Å, respectively.



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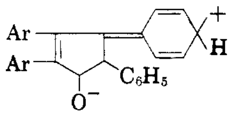

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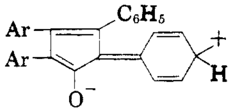
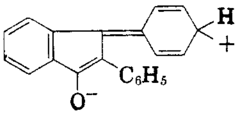
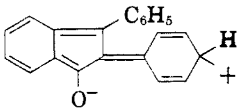


IVb



IIIa



IIIb

TABLE I

Properties of Arylmethylenephthalides

Ar_1	Yield, %	Crystallized from	M.p., °C.	Analysis C Calc'd	Analysis C Found	Analysis H Calc'd	Analysis H Found	Ultraviolet spectra[a] λ_{max} [A] (log ϵ)
C_6H_5								2280 (4.18); 2520 (4.02); 2950 (4.30); 3080 (4.28); 3380 (4.30)[b]
p-BrC_6H_4	46	Isobutyl alcohol	162[c]					2330 (4.18); 2540 (4.08); 2970 (4.38); 3100 (4.36); 3410 (4.44)
p-$CH_3OC_6H_4$	54	*n*-Butanol	145	76.2	76.5	4.8	4.8	2350 (4.26); 3250 (4.22); 3540 (4.34)
o-Cl-C_6H_4	67	*n*-Butanol	163	70.3	70.0	3.5	3.8	2450 (3.97); 2950 (4.10); 3350 (4.15)
α-$C_{10}H_7$	80	Acetic acid; ethyl acetate	179[d,e]	83.8	83.6	4.4	4.6	2610 (4.19); 3645 (4.27)
β-$C_{10}H_7$	51	*n*-Butanol	171[f]	83.8	83.5	4.4	4.4	2780 (4.36); 2875 (4.45); 3540 (4.51)

[a] All spectra have been determined in 96% ethyl alcohol. [b] Ref. 12. [c] Ref. 13. [d] The substance has a slight green fluorescence; it dissolves in concentrated sulfuric acid with a yellow color and an intense green fluorescence. [e] In one experiment, a second compound was isolated, from glacial acetic acid in golden-yellow leaflets, m.p. 157–158°. U. V. spectrum: 2600 (4.30); 3620 (4.26). It has not been decided whether this was an isomer or a polymorphic modification of the substance of m.p. 179°; the identity of the spectra rather points to the second alternative. *Anal.* Calc'd for $C_{19}H_{12}O_2$: C, 83.8; H, 4.4. Found: C, 83.6; H, 4.6. [f] Ref. 14.

Becker and co-workers[19–21] have interpreted the two main bands in the spectra of the analogously constituted tetraarylcyclopentadienones (IV) as representing the "absorption paths" IVa and IVb, respectively. The same possibility would, *a priori*, exist for III, *viz.* in the modifications IIIa and IIIb; this would imply that substitution in the 3-phenyl group of 2,3-diphenylindone would mainly affect the 2560 Å band, substitution in the 2-phenyl group the 4400 Å band.

The data of Table II indicate that at best the general trend is in accord with the predictions; however, the deviations are so numerous that one cannot describe the absorption of the diarylindones by simple formulae of the type (IIIa, IIIb). There is also no influence of the aryl groups in the 2- and 3-positions on the stretching frequency of the carbonyl group.

EXPERIMENTAL

p-Bromophenylacetic acid was prepared according to Dippy and Williams[22] from *p*-bromobenzyl chlor-

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TABLE II

2,3-DIARYLINDONES (III)

Ar^1	Ar^2	Formula	Crystallized from	M.p., °C.	C		H		Absorption spectrum (in alcohol) λ_{max} [Å] (log ϵ)	Shift (Å) of the 2560 Å band[a]		Shift (Å) of the 4400 Å band		Infrared spectrum[b] (cm.$^{-1}$, ±3 cm.$^{-1}$)
					Calc'd	Found	Calc'd	Found		Predicted	Found	Predicted	Found	
C_6H_5	C_6H_5	$C_{21}H_{14}O$		151° (red)					[2340 (4.48)] 2560 (4.50); 4400 (3.24)[c]					1715[d]
C_6H_5	p-OCH_3-C_6H_4	$C_{22}H_{16}O_2$	Ethanol	120[k, l] (crimson-red)	84.6	84.2	5.1	5.1	2630 (4.50); 4480 (3.40)	+	+ 70	0	+ 80	1712
p-OCH_3-C_6H_4	C_6H_5	$C_{22}H_{16}O_2$	Isopropyl alcohol	118–119[k] (red)	84.6	84.6	5.1	5.1	2650 (4.60); 4600 (3.36)	0	+ 90	+	+200	1713
C_6H_5	p-Br-C_6H_4[e]	$C_{21}H_{13}BrO$	Butyl alcohol	170 (dark brown-red)	70.0	70.4	3.6	4.0	2600 (4.58); 4360 (3.30)	(+)	+ 40	(0)	− 40	1711
p-Br-C_6H_4	C_6H_5	$C_{21}H_{13}BrO$	Isopropyl alcohol	145 (orange-red)	70.0	70.0	3.6	3.8	2650 (4.59); 4400 (3.36)	(0)	+ 90	(+)	0	1715
C_6H_5	o-Cl-C_6H_4	$C_{21}H_{13}ClO$	Isopropyl alcohol	183–184 (orange-yellow)	79.7	79.5	4.1	4.2	2600 (4.60); 4350 (3.26)	−	+ 40	0	− 50	1720
o-Cl-C_6H_4	C_6H_5	$C_{21}H_{13}ClO$	Isopropyl alcohol	120 (orange-yellow)	79.7	79.5	4.1	4.2	2475 (4.57); 4150 (3.19)	0	− 85	−	−250	
C_6H_5	o-CH_3-C_6H_4[f]	$C_{22}H_{16}O$	Isopropyl alcohol; cyclohexane	125 (orange-yellow)					2620 (4.61); 4350 (3.24)[h]	−	+ 60	0	− 50	1716
C_6H_5	α-$C_{10}H_7$[g]	$C_{25}H_{16}O$	Isopropyl alcohol	180 (bichromate-colored)					[2230 (4.84)] 2640 (4.55); 4160 (3.53)	0	+ 80	−	−240	1714
α-$C_{10}H_7$	C_6H_5	$C_{25}H_{16}O$	Isopropyl alcohol	156 (ruby-red)	90.4	90.3	4.8	4.9	[2240 (4.30)] 2860 (4.28); 4320 (3.18)	−	+300	0	− 80	1717
C_6H_5	β-$C_{10}H_7$	$C_{25}H_{16}O$	Acetic acid	99[m] (orange-red)	90.4	90.1	4.8	5.0	[2210 (4.92)] 2625 (4.66); [3150 (3.90)] 4450 (3.38)	+	+ 65	0	+ 50	1715
β-$C_{10}H_7$	C_6H_5	$C_{25}H_{16}O$	Nitromethane	159–160 (dark-red)	90.4	90.1	4.8	4.9	2660 (4.15); 4480 (2.84)[i]	0	+100	+	+ 80	1714

[a] + indicates a bathochromic; − a hypsochromic shift. [b] Measured in carbon tetrachloride; only 2-phenyl-3-(p-bromophenyl)indone was measured in chloroform. See M.-L. Josien and N. Fuson, *Compt. rend.*, **236**, 1879 (1953). [c] E. Bergmann, E. Fischer, and J. H. Jaffe, *J. Am. Chem. Soc.*, **75**, 3230 (1953). [d] E. Bergmann, *et al.*, *Bull. soc. chim. France*, **18**, 661 (1951); *J. Chim. Phys.*, **49**, 537 (1952). [e] Ref. 14. [f] Ref. 2. [g] Ref. 4. [h] In chloroform: 2650 (4.76); 4350 (3.22). [i] In chloroform: 2670 (4.76); 4550 (3.42). [k] The two ketones gave a very pronounced depression of the mixture m.p. [l] Ref. 3a. [m] We have been unable to duplicate the melting point indicated by Dalev (ref. 3b).

ide[23,24]; it was recrystallized from 50% alcohol and melted at 114°.

Analogously, α-naphthylacetic acid was obtained from 1-chloromethylnaphthalene.[25,26] Recrystallized from water it had m.p. 132°. For the preparation of β-naphthylacetic acid, the Willgerodt-Kindler rearrangement of 2-acetylnaphthalene[27] was preferred; recrystallization from benzene gave m.p. 137°.

p-Methoxyphenylacetic acid, m.p. 85–86°, was obtained[28,29] from 2-phenyl-4-(*p*-methoxybenzylidene)oxazolone by alkaline hydrolysis and oxidation with hydrogen peroxide; purification by distillation *in vacuo:* b.p. 160–170°/26 mm.

For the synthesis of *o*-chlorophenylacetic acid, *o*-chlorotoluene was chlorinated with sulfuryl chloride and benzoyl peroxide[23,24] and the *o*-chlorobenzyl chloride so obtained was treated successively with potassium cyanide in dilute alcohol (*o*-chlorobenzyl cyanide, b.p. 141°/12 mm.)[30] and dilute alkali.[31]

The 3-arylmethylenephthalides (I) were obtained by the method described for benzylidenephthalide.[11] The preparation of the 2,3-diarylindones (III) may be illustrated by the following representative examples.

2-(p-Bromophenyl)-3-phenylindone. To a Grignard solution, prepared from 2 g. of magnesium and 8.6 ml. of bromobenzene, 5 g. of powdered *p*-bromobenzylidenephthalide was added and the reaction mixture was refluxed for 4 hours and decomposed with ice and ammonium chloride. The residue of the ethereal solution was distilled with steam and the nondistillable product was taken up in ether again. After washing and drying, a red resin remained which did not crystallize and was, therefore, subjected to evaporative distillation at 2 mm. pressure. The distillate was triturated with ethyl acetate, whereupon it crystallized completely. From isopropyl alcohol, it formed beautiful, orange-red crystals, m.p. 145°. Yield, 5 g. (83%).

2-Phenyl-3-(o-chlorophenyl)indone. The reaction product from 2 g. of magnesium, 17.9 g. of *o*-chloroiodobenzene (b.p. 110°/16 mm.), and 5 g. of benzylidenephthalide was decomposed with dilute sulfuric acid and ice and the ether residue was distilled *in vacuo;* b.p. 260–270°/5 mm. The resinous distillate was triturated with a mixture of acetone and alcohol at 0° and the solid product was recrystallized from butyl alcohol; orange-yellow leaflets, m.p. 183–184°. Yield, 4.5 g. (63%).

2-(β-Naphthyl)-3-phenylindone. A suspension of 6.1 g. of β-naphthylmethylenephthalide in benzene was added to the Grignard solution, prepared from 2 g. of magnesium and 8.6 ml. of bromobenzene. The mixture was refluxed for 4 hours and the resulting clear solution was poured onto ice. The mixture was black and turned suddenly orange-red. Dilute sulfuric acid was added in a slight excess, whereupon an almost colorless product began to crystallize. It was collected (4.6 g.; 60%) and recrystallized from toluene to give slightly yellowish prisms, which melt at 172° to a deep-red liquid, but redden somewhat below this temperature. The analysis and the infrared spectrum (mull in paraffin oil; *vide supra*) pointed to the formula of 2-(β-naphthylacetyl) benzophenone (as II).

Anal. Calc'd for $C_{25}H_{18}O_2$: C, 85.7; H, 5.1. Found: C, 85.6; H, 5.2.

The original benzene-ether solution was dried and evaporated, and the residue was distilled *in vacuo*. At 260–270°/2 mm., a red resin was obtained which solidified upon trituration with acetone and was recrystallized from nitromethane. The indone formed dark red, brilliant prisms, m.p. 159–160°.

Anal. Calc'd for $C_{25}H_{16}O$: C, 90.4; H, 4.8. Found: C, 90.7; H, 4.8.

From the nitromethane mother liquor, upon evaporation, a mixture of the indone with the diketone was obtained, which could easily be separated mechanically.

The same indone was obtained when the substance of m.p. 172° was heated for one hour at 200–210°.

2-Phenyl-3-(o-tolyl)indone. The product obtained from 2 g. of magnesium, 9.2 ml. of *o*-bromotoluene, and a benzene suspension of 5 g. of benzylidenephthalide (refluxing for 6 hours) was decomposed with ice-cold dilute sulfuric acid. When the orange ether layer was dried and evaporated, a partly solid residue was obtained. This was subjected to distillation under 0.7 mm. pressure. At 200–220° a dark red oil was obtained which crystallized when kept at 0° with methanol and a little acetone. From cyclohexane it gave orange-yellow needles of m.p. 125° (literature[3a]: m.p. 123–125°). Yield, 4 g. (60%).

When the reaction was carried out without benzene, the same procedure gave a colorless compound which crystallized spontaneously from the ethereal solution after decomposition. More of the same product was obtained when the ethereal mother liquor was evaporated and the resulting reddish crystalline mass was triturated with methanol. The methanol solution left, upon evaporation, a little of the above indone, m.p. and mixture m.p. 123–124°. The colorless product was recrystallized from butanol and had m.p. 176° (dec.; orange-red melt). Its analysis and properties proved that it is 2-(*o*-tolylacetyl)benzophenone.

Anal. Calc'd for $C_{22}H_{18}O_2$: C, 84.1; H, 5.7. Found: C, 84.0; H, 5.6.

When this compound was heated for 1 hour at 190°, a red melt was obtained which crystallized upon trituration with hot methanol. From isopropyl alcohol or ligroin, m.p. 125°.

2-Phenyl-3-(β-naphthyl)indone. The crude product obtained from 1.4 g. of magnesium, 10.3 g. of β-bromonaphthalene, and 3.4 g. of benzylidenephthalide (refluxing for 4 hours; decomposition with ice and dilute sulfuric acid; filtration of 0.5 g. of β,β'-dinaphthyl, from isopropyl alcohol, m.p. and mixture m.p. 181°) was subjected to evaporative distillation in a vacuum (0.7 mm.). The dark-red distillate crystallized upon trituration with glacial acetic acid and was recrystallized from the same solvent. Thus, a mixture of dark-red and of yellowish prisms was obtained; they were separated mechanically and again were recrystallized from glacial acetic acid. The yellowish prisms melted at 184–185° (dark red melt) and were according to the analysis 2-(phenylacetylphenyl) β-naphthyl ketone; their solutions in butyl alcohol showed an intense fluorescence.

Anal. Calc'd for $C_{25}H_{18}O_2$: C, 85.7; H, 5.1. Found: C, 85.8; H, 4.8.

The orange-red prisms of the described indone melted at 99°. Dalev[3b] recently reported m.p. 132°.

Anal. Calc'd for $C_{25}H_{16}O$: C, 90.4; H, 4.8. Found: C, 90.5; H, 4.9.

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