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Diaryliodonium Salts. XVII. The Phenylation of 1,3-Indandiones[1,2]

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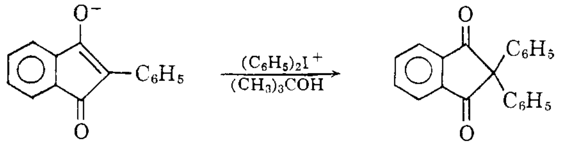
Previous work has shown that the anions of acidic di- and triketones in *t*-butyl alcohol can be phenylated by diphenyliodonium salts. Under these conditions 1,3-indandione and 2-phenyl-1,3-indandione (I) are both converted to 2,2-diphenyl-1,3-indandione (II), the latter reaction occurring in 93% yield. The following mechanism is proposed: electron transfer within an ion pair from a carbanion (R^-) to an iodonium ion ($Ar\overset{+}{I}Ar$) to give a radical pair, the members of which largely give ArR. In *t*-butyl alcohol there is formed some reduced product, ArH; more is formed in prim. and sec. alcohols. Some radicals escape from the solvent cage, combining later to form ArR, RR and ArAr. The radical scavenger, oxygen, to which the carbanion of I is inert, reduces the yield of phenylated product II to 53%, while styrene reduces the yield of II to 70% and gives polymers of low molecular weight containing carbonyl groups.

Introduction.—A previous article[4] from this Laboratory reported the phenylation of the anions of dimedone,[5] dibenzoylmethane and tribenzoylmethane with diphenyliodonium salts. Yields were best in *t*-butyl alcohol, as in 1° and 2° alcohols dehydrogenation of the solvent accompanied reduction of the iodonium salt. A major aim of the present work has been to elucidate the mechanism of this phenylation by observing the change in the product distribution effected by the radical scavengers oxygen and styrene. The system chosen was that of the anions of 1,3-indandione and its 2-phenyl and 2-carbethoxy derivatives with diphenyliodonium chloride in *t*-butyl alcohol.

Reaction of 2-Phenyl-1,3-indandione.—A solution containing the sodium salt of 2-phenyl-1,3-indandione[6] (I) and an equivalent of diphenyliodonium chloride[7] was heated under reflux to give as the major product the known non-acidic 2,2-diphenyl-1,3-indandione[8] (II).

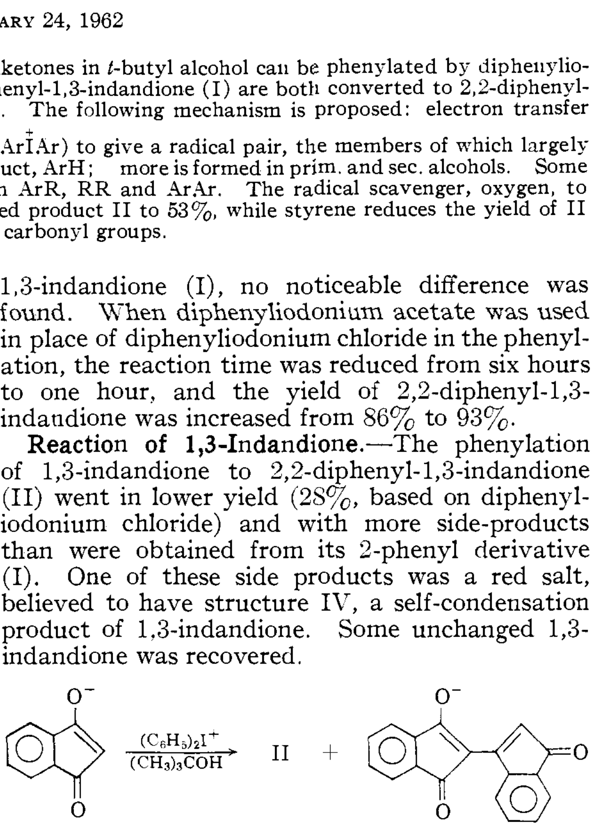


Anion of I II

Other products were iodobenzene, biphenyl and, in small amounts, a dehydrodimer of I and a higher melting compound. While it seems likely that this dehydrodimer was formed by coupling of 2-phenyl-1,3-indandion-2-yl free radicals, the structure has not yet been definitely assigned. Further work on the dehydrodimer and the higher-melting compound will be reported later.

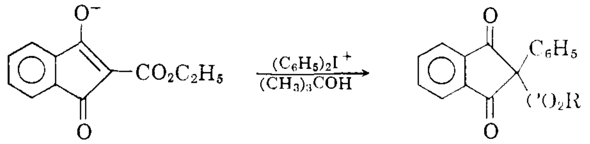
When lithium *t*-butoxide was used in place of sodium *t*-butoxide in the phenylation of 2-phenyl-1,3-indandione (I), no noticeable difference was found. When diphenyliodonium acetate was used in place of diphenyliodonium chloride in the phenylation, the reaction time was reduced from six hours to one hour, and the yield of 2,2-diphenyl-1,3-indandione was increased from 86% to 93%.

Reaction of 1,3-Indandione.—The phenylation of 1,3-indandione to 2,2-diphenyl-1,3-indandione (II) went in lower yield (28%, based on diphenyliodonium chloride) and with more side-products than were obtained from its 2-phenyl derivative (I). One of these side products was a red salt, believed to have structure IV, a self-condensation product of 1,3-indandione. Some unchanged 1,3-indandione was recovered.



III IV

Reaction of Ethyl 1,3-Indandione-2-carboxylate.—It was hoped that the phenylation of the 2-carbethoxy analog would give the phenylated ester, from which 2-phenyl-1,3-indandione (I) could be obtained by hydrolysis. This was, indeed, one of the reaction paths; 23% of mixed ethyl and *t*-butyl 2-phenyl-1,3-indandione-2-carboxylates was isolated along with 6% of the diphenyl derivative II. Such products could be explained by ester interchange, decarboxylation and phenylation.



V

VI R = ethyl
VII R = *t*-butyl

Experiments Suggesting Free Radical Intermediates.—Several reactions of the anion of 2-phenyl-1,3-indandione with diphenyliodonium chloride suggested that free radicals are formed as intermediates in the phenylation of carbanions. The first result suggesting this was dehydrogenation of isopropyl alcohol to acetone, with concomitant formation of benzene[9]; the yield of phenylated product fell to

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[1] This article is taken in part from the thesis of Suzanne A. Galton, submitted in partial fulfillment of the requirements of the degree of Master of Science in Chemistry.

[2] Preceding paper: F. M. Beringer and I. Lillien, *J. Am. Chem. Soc.*, **82**, 5141 (1960).

[3] (a) Eastman Kodak Research Fellow, 1961–1962; (b) U. S. Rubber Co. Fellow, 1960–1962.

[4] F. M. Beringer, P. S. Forgione and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960).

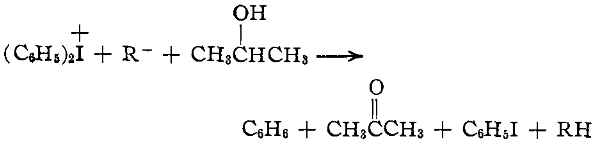
[5] The phenylation of dimedone has also been reported by Russian workers: O. Neilands, G. Vanags and F. Gudriniece, *J. Gen. Chem. USSR*, **28**, 1201 (1958); *C. A.*, **52**, 19988 (1958).

[6] W. Dieckmann, *Ber.*, **47**, 1439 (1914).

[7] F. M. Beringer, E. J. Geering, I. Kuntz and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

[8] (a) R. Schönberg and R. Moubasher, *J. Chem. Soc.*, 71 (1943); (b) R. Moubasher, *J. Am. Chem. Soc.*, **73**, 3246 (1951).

[9] Similar dehydrogenations of prim. and sec. alcohols in the attempted phenylation of dimedone have been previously reported (ref. 4).



$$(C_6H_5)_2\overset{+}{I} + R^- + CH_3\overset{\overset{OH}{|}}{C}HCH_3 \longrightarrow C_6H_6 + CH_3\overset{\overset{O}{\|}}{C}CH_3 + C_6H_5I + RH$$

49%. This observation was rationalized most easily by assuming the intermediacy of phenyl free radicals and led to the addition of radical-scavengers to phenylation reactions. In one case styrene was added to the solution of the anion of 2-phenyl-1,3-indandione and diphenyliodonium chloride in *t*-butyl alcohol. Reaction under reflux gave a decreased yield (70%) of phenylated product (II) as well as low polymers of styrene.[10] The infrared spectra of these polymers showed the presence of carbonyl groups, not removable by precipitation. This result can be rationalized by assuming that the carbanion (R^-) was oxidized to a free radical ($R\cdot$), which initiated polymerization of styrene.

Finally, it was shown that although oxygen does not oxidize the carbanion (R^-) at 80°, oxygen bubbled through a boiling solution of the carbanion and diphenyliodonium chloride in *t*-butyl alcohol reduced the yield of phenylated product to 53%. These results are summarized in Table I.

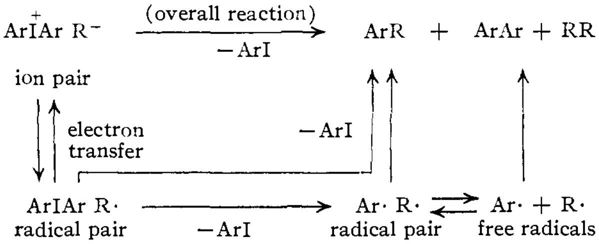
TABLE I

2-SUBSTITUTED 1,3-INDANDIONES WITH DIPHENYLIODONIUM CHLORIDE AND SODIUM *t*-BUTOXIDE IN *t*-BUTYL ALCOHOL

Carbanion *R'*	Phenylated prod., ArR	Yields, % ArR	ArI	ArH[a]	ArAr[b]	RR[a]	Time[c]
V	II	6[d]	30	8	+	+	3-5 days
	VI	10[d]					
	VII	13[d]					
III	II	28	51	12	+	+	10 min.
I[e]	II	86	28	20	+	+	6 hr.
I[f]	II	93	35	+		+	2 hr.
I[g]	II	70	66	+		+	6 hr.
I[h]	II	53	71	+		+	6 hr.

[a] Determined by ultraviolet spectroscopy. The notation + indicates that the compound was present but not measured. [b] Detected by paper chromatography. [c] Time of reaction under reflux. [d] Determined by quantitative paper chromatography and ultraviolet spectroscopy. [e] No significant change on replacing sodium with lithium *t*-butoxide. [f] Diphenyliodonium chloride was replaced by the acetate. [g] Run in the presence of styrene; see Experimental. [h] Run in the presence of oxygen; see Experimental.

Mechanism of the Phenylation of Carbanions.—A tentative mechanism now proposed for the phenylation of carbanions may allow explanation of the above observations.



It is proposed that electron transfer from carbanions to iodonium ions gives radical pairs. The members of such radical pairs in *t*-butyl alcohol largely react together, either by radical displacement of $R\cdot$ on diphenyliodine[11] or by coupling of $R\cdot$ and phenyl radicals. Some free radicals, formed by diffusing apart of the members of the radical pairs, later couple to give ArR, ArAr and RR.

Since the yield of phenylated product (ArR) can be as high as 93%, it seems that if the above mechanism is correct, most of the yield of ArR is accounted for by reaction within the radical pair, and only a small amount arises from recombination of free radicals.

It has been shown that the presence of isopropyl alcohol, of styrene and of oxygen depresses the yield of ArR to 70% or below. Therefore, these three reagents must be somewhat reactive to radical pairs as well as to free radicals.

Experimental[12]

Starting Materials and Reference Compounds. Ethyl 1,3-Indandione-2-carboxylate.—The sodium salt of this diketo ester was prepared by a modification of the procedures of Wislicenus[13] and of Fieser.[14] To a solution of 48.6 g. (2.1 g.-atoms) of sodium in 500 ml. of absolute ethanol a solution of 294 ml. (1.5 moles) of diethyl phthalate in 600 ml. of ethyl acetate (6 moles) was added with stirring. After the clear yellow solution had been concentrated to a thick sirup by distillation at atmospheric pressure, more ethyl acetate was added and at the same time removed by distillation, until a total of 2.5 liters of ethanol and ethyl acetate had been removed. The crystals collected by suction filtration of the thick suspension were washed with ethyl acetate and dried *in vacuo* to yield 153 g. (0.64 mole, 43%) of the yellow **sodium salt of ethyl 1,3-indandione-2-carboxylate.** Recrystallization from ethanol in a Soxhlet extractor gave yellow crystals which did not melt at 300° but darkened above that temperature. The ultraviolet absorption spectrum of the yellow salt in ethanol had bands, given as λ_{max} (ϵ_{max}): 215 (25,200), 221 (24,900), 252 (20,200), 262 (31,400), 272 (44,800), 393 (4050), 305 (6060) and 318 mμ (5410).

Anal. Calcd. for $C_{12}H_9O_4Na$: C, 60.00; H, 3.78. Found: C, 59.77; H, 3.68.

Acidification of the yellow salt with 3 *N* hydrochloric acid at 0° gave, after collection, washing and drying *in vacuo* over phosphorus pentoxide, **ethyl 1,3-indandione-2-carboxylate** as yellow needles, m.p. 78-79° (reported[14] m.p. 75-78°), pK_a in 50% ethanol-water 2.55. The ultraviolet absorption spectrum in ethanol had bands, given as λ_{max} (ϵ_{max}): 263 (32,500), 273 (45,000), 296 (3400), 306 (4500) and 318 mμ (3960).

The free diketoester is apparently unstable *in vacuo* at room temperature.

1,3-Indandione was prepared by the acidification, hydrolysis and decarboxylation of ethyl 1,3-indandione-2-carboxylate. Thus, 75 g. (0.31 mole) of the sodium salt was stirred into a liter of 3 *N* hydrochloric acid, with the temperature rising to 80°. The mixture was heated with

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(10) Similar reaction mixtures from which diphenyliodonium chloride was omitted gave no polystyrene.

(11) The formation of diphenyliodine in electroreductions [H. E. Bachofner, F. M. Beringer and L. Meites, *J. Am. Chem. Soc.*, **80**, 4269 (1958)] and the possible role of diphenyliodine as a reaction intermediate [F. M. Beringer, E. M. Gindler, M. Rappoport and R. J. Taylor, *ibid.*, **81**, 351 (1959)] have been previously discussed.

(12) Analyses were performed by Schwarzkopf Micro-analytical Laboratories, Woodside, N. Y., and by the analytical laboratories of Chas. Pfizer and Co., Inc. Infrared spectra were taken on a Baird-Atomic double beam recording spectrophotometer, model No. AB, and a Perkin-Elmer Infracord spectrophotometer, model No. 137. Ultraviolet spectra were taken on a Cary model 11 recording spectrophotometer. Melting points were taken in capillary tubes and were corrected.

(13) J. Wislicenus, *Ann.*, **246**, 307 (1888).

(14) L. Fieser, "Experiments in Organic Chemistry," revised Third Edition, D. C. Heath and Co., Boston (1957), p. 123.

stirring until evolution of carbon dioxide ceased (~10 min.). The light tan solid collected by filtration of the chilled reaction mixture was washed with water and dried *in vacuo* to give 46 g. (0.31 mole, 100%) of crude **1,3-indandione**, m.p. 127–128°. Recrystallization from benzene gave 35 g. (0.24 mole) of 1,3-indandione, m.p. 129.5–130.5°, while sublimation raised the m.p. to 132–133°, reported[14] m.p. 131.5–132.5°. The pK_a in 50% ethanol–water was 6.55. In ethanol the bands in the ultraviolet absorption spectrum, given as λ_{max} (ϵ_{max}), were 223 (44,400), 250 (14,500) and 259 mμ (10,160); while in 0.1 *N* sodium ethoxide in ethanol the bands were 249 (36,400) and 259 mμ (33,400).

2-Phenyl-1,3-indandione (I) was prepared by the following modification of the method of Dieckmann.[15] To a solution of 12.5 g. (0.55 g.-atom) of sodium in absolute ethanol there was added with stirring a solution of 67 g. (0.5 mole) of phthalide and 53 g. (0.5 mole) of benzaldehyde in 300 ml. of absolute ethanol. After the deep red solution had been boiled under reflux for 30 minutes and most of the ethanol had been removed by distillation under reduced pressure, the residue was diluted with 500 ml. of water, cooled and extracted three times with chloroform to remove unchanged starting materials. When the chilled aqueous phase was acidified, the red color was discharged, and a light tan solid was formed. This precipitate was collected, washed with water and dried to yield 40.5 g. (0.182 mole, 36%), of crude **2-phenyl-1,3-indandione**, m.p. 140–142°. The solvent-wet crystals still in the Büchner funnel after a second recrystallization from ethanol were washed with petroleum ether to remove the red color which adhered to the crystals. The shiny white flakes of 2-phenyl-1,3-indandione so obtained had a m.p. 147–148°, raised by sublimation to 150–151°, reported[15] m.p. 149°. The pK_a was 4.4 in 50% ethanol–water. Values of λ_{max} (ϵ_{max}) in ethanol were 225 (28,500), 278 (21,000), 287 (17,400), 324 (4200), 336 (4700) and 350 mμ (3050); values in 0.1 *N* sodium ethoxide in ethanol were 278 (25,800), 287 (32,000), 323 (12,100), 335 (14,600) and 349 mμ (10,880).

2,2-Diphenyl-1,3-indandione (II).—Ten grams (56 mmoles) of ninhydrin was sublimed *in vacuo* at 190° to yield 8.4 g. (52 mmoles, 94%) of **1,2,3-indantrione**, purple crystals, m.p. 254–255°, reported[8a] 255°. To a suspension of this product in 50 ml. of benzene there was slowly added with stirring 20 ml. of 30% fuming sulfuric acid; the temperature of the reaction mixture was held between 0° and 10°. After 45 minutes the dark brown reaction mixture was poured over ice, and the two-phase system was extracted with chloroform. The residue from concentration of the dried chloroform extract was triturated with ether, giving white crystals. These were collected, washed and dried to yield 5.0 g. (17 mmoles, 31%) of **2,2-diphenyl-1,3-indandione**, m.p. 117–119°, raised by two crystallizations from ethanol to 119–120°, further raised by sublimation to 125°, reported[8b] m.p. 118°. The bands of the ultraviolet absorption spectrum in ethanol, as λ_{max} (ϵ_{max}), were 226 (55,000), 245 (15,000), 303 (850), 331 (330) and 346 mμ (377).

Diphenyliodonium Acetate.[16]—To a solution of 94.8 g. (0.3 mole) of diphenyliodonium chloride in 750 ml. of acetic acid at 60° there was added with vigorous stirring a hot solution of 50.1 g. (0.3 mole) of silver acetate in 750 ml. of acetic acid and 250 ml. of acetonitrile. After the mixture was cooled to 0°, the silver chloride was removed by filtration through Celite, and the filtrate was concentrated at 40° under vacuum to a viscous oil. To this residue 1 liter of ethyl ether was added in 200-ml. portions with vigorous shaking. The white granules formed were filtered, washed with ether and dried to give 99 g. of crude **diphenyliodonium acetate**, m.p. 105–112°. One recrystallization from *t*-butyl alcohol–hexane yielded 70 g. (0.205 mole, 68%) of diphenyliodonium acetate, m.p. 132–137°, which gave negative tests for silver and chloride ions. Two more recrystallizations from *t*-butyl alcohol–hexane containing 1% acetic acid raised the m.p. to 146–147°.

Anal. Calcd. for $C_{14}H_{13}O_2I$: C, 49.43; H, 3.85; I, 37.31; neut. equiv., 340.1. Found: C, 49.31; H, 4.10; I, 37.75; neut. equiv., 340 ± 2 (non-aqueous titration with *p*-toluenesulfonic acid).

Phenylation of 2-Phenyl-1,3-indandione(I).—To a solution of 2.55 g. (110 mg.-atoms) of sodium in 1.2 liters of *t*-butyl alcohol (freshly distilled from calcium hydride), 20 g. (90 mmoles) of 2-phenyl-1,3-indandione was added with stirring. After the mixture had been heated, the blood-red solution was cooled, and 28.5 g. (90 mmoles) of diphenyliodonium chloride[7] was added. The reaction was boiled under reflux (nitrogen) for 6 hours, at which time a sample gave no precipitate with a potassium iodide solution, indicating no unreacted diphenyliodonium ion.

Filtration of the brown mixture gave 10 g. of a solid containing chloride ion but no diphenyliodonium ion; the solid was not completely soluble in water. From these tests and from the fact that the theoretical amount of sodium chloride formed should be 5.25 g., it was concluded that the solid was a mixture of sodium chloride and some organic material.

The filtrate was concentrated to a small volume *in vacuo* while the distillate was collected in a trap cooled by Dry Ice–acetone. The residue was combined with the 10 g. of solid filtered from the reaction mixture and was suspended in 400 ml. of 1 *N* sodium hydroxide to remove any acidic components. The alkaline mixture was extracted with about 1.5 liters of methylene chloride, which in turn was extracted with more 1 *N* sodium hydroxide until the aqueous phase was practically colorless. The combined aqueous phase was backwashed thoroughly with methylene chloride, acidified with concentrated hydrochloric acid and extracted with methylene chloride. This extract, constituting the acidic fraction, was concentrated to dryness *in vacuo* to yield 2.58 g. (12.9 mmoles, 11.6%) of unchanged **2-phenyl-1,3-indandione** (I).

The combined methylene chloride extract containing the neutral fraction was dried over anhydrous magnesium sulfate and concentrated to dryness *in vacuo*. The residue was chromatographed on a 500-g. Florisil (60/100 mesh) column prepared in petroleum ether and was eluted successively with petroleum ether, benzene, methylene chloride, ethyl acetate and methanol.

The petroleum ether fraction, after removal of solvent, was combined with the trapped *t*-butyl alcohol and distilled through a fractionating column at atmospheric pressure to yield 5.21 g. (25.5 mmoles, 28%) of **iodobenzene**, identified by infrared spectrum.

The benzene fraction after evaporation of the solvent gave 21.5 g. (72 mmoles, 86% yield) of oily yellow prisms of crude **2,2-diphenyl-1,3-indandione** (II). Two crystallizations from ethanol yielded 14 g. of pure material, m.p. 122–123°, with no depression of melting point when mixed with an authentic sample. The infrared spectrum was identical to that of an authentic sample. Paper chromatography of the crude material in a hexane–methyl Carbitol system showed also the presence of biphenyl.

From the methanol fraction 0.23 g. of a light yellow solid was isolated, which after two recrystallizations from ethanol–benzene gave white crystals, m.p. 320°, presently under investigation. The remaining fractions yielded no isolable materials.

When the phenylation was run with one equivalent of sodium, and the reaction worked up according to the above procedure, besides the very high melting material isolated as before, a dehydrodimer of m.p. 206–208° was obtained.[17] The infrared spectrum of this material is similar to that of the 2-phenyl-1,3-indandione. The yield of phenylated product II dropped to 75.5%, and 21% of unchanged starting material I was recovered.

A series of experiments showing the effect of changing the metal, the diphenyliodonium anion, the molar equivalent of reactants and solvent, as well as the presence of oxygen and styrene on the phenylation of 2-phenyl-1,3-indandione are summarized in Table II. All the reactions were worked up according to the above procedure.

Phenylation of 1,3-Indandione (III).—To a solution of 4.7 g. (220 mg.-atoms) of sodium in 1.2 liters of *t*-butyl alcohol (freshly distilled from calcium hydride) there was added with stirring 25 g. (171 mmoles) of recrystallized 1,3-indandione. A red solution was obtained from which a brick-red solid precipitated immediately. After 10

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(15) W. Dieckmann, *Ber.*, **47**, 1439 (1914).

(16) M. D. Yudis, Ph.D. Dissertation, Polytechnic Institute of Brooklyn, 1963.

(17) F. Nathanson [*Ber.*, **26**, 2582 (1893)] prepared a dehydrodimer, m.p. 208°, from 2-phenyl-1,3-indandione by treatment with aqueous nitrous acid or with ethanolic sodium nitrite. He formulated the compound as the C–C dehydrodimer, bis-(2-phenyl-1,3-indandion-2-yl).

TABLE II

A SUMMARY OF CONDITIONS AND RESULTS OF THE PHENYLATION OF 2-PHENYL-1,3-INDANDIONE[a]

Ar_2I^+		Mmoles		Mg.-atom	Refl.,	Recov.	Product	ArI,	Dimer m.p. 208°,	Cpd. m.p. 320°,
X^-	Mmoles	I	Metal	metal	hr.	I, %	II, %	%	mg.	mg.
Cl^-	90	90	Na	110	6	11.6	86	28	..	230
Cl^-	38.6	38.5	Na	38.6	6	21	75.5	30	87	73
Cl^-	25	25	Li	25.2	5.5	7.2	86	23		60
Cl^{-b}	50	50	Na	55	6	..	53	71	..	50
Cl^{-c}	20	20	Na	21	6	10	70	66	..	..
Cl^{-d}	25	25	Na	25.2	6	19	49	tr.	..	270
AcO^-	55	50	Na	50	2	2.4	93	35	62	23
AcO^-	7.25	6.5	Li	6.5	1	3.5	92.4	54	..	tr.

[a] The solvent used was *t*-butyl alcohol unless otherwise stated; Ar = phenyl. [b] Oxygen was bubbled through during the entire reaction. In addition to the above products, from the acidic fraction some phenol was isolated as the tri- and tetrabromide. [c] Run in the presence of 20 mmoles of styrene. Samples taken during the first hour of reflux gave a blue color with a 1% aqueous solution of N,N,N′,N′-tetramethyl-*p*-phenylenediamine. From the neutral methylene chloride fraction 0.56 g. of an amorphous solid, m.p. 100–110°, was obtained and purified by precipitating it twice from methylene chloride with methanol. The infrared spectrum showed the characteristic peaks of polystyrene, plus two carbonyl peaks characteristic of the indandione structure. [d] Isopropyl alcohol was used as solvent. At the end of the reaction the solvent was fractionally distilled. The distillate contained 9.5% benzene, determined by ultraviolet spectroscopy, and 19% acetone, determined as its 2,4-dinitrophenylhydrazone derivative.

minutes at reflux and after cooling, 54 g. (171 mmoles) of diphenyliodonium chloride was added. Ten minutes heating gave a clear blood-red solution, which gave a negative test for diphenyliodonium chloride. The reaction was worked up according to the above-outlined procedure.

From the acidic fraction 15.4 g. of a red solid was isolated; structure IV has been tentatively proposed. It was soluble in water and alcohols and on treatment with hydrochloric acid gave a brown precipitate. The infrared spectrum of this compound indicates the presence of a carboxylic acid or a highly conjugated enol. Also, 2 g. (8%) of crude unchanged 1,3-indandione was recovered.

The neutral fraction yielded 9.1 g. (51%) of **iodobenzene** and 14.3 g. (28%) of **2,2-diphenyl-1,3-indandione (II)**. Paper chromatography in a hexane–methyl Carbitol system also showed the presence of biphenyl.

Phenylation of the Sodium Salt of Ethyl 1,3-Indandione-2-carboxylate (V).—A mixture of 25.0 g. (104 mmoles) of recrystallized sodium salt of ethyl 1,3-indandione-2-carboxylate and 33.0 g. (104 mmoles) of diphenyliodonium chloride in 1.25 liters of freshly distilled *t*-butyl alcohol was boiled under reflux in a nitrogen atmosphere for 3 days; no unreacted diphenyliodonium chloride was found. At no time was the reaction homogeneous, as both reactants are only slightly soluble in *t*-butyl alcohol. During this period the color of the reaction mixture changed from bright yellow to deep red-brown. The mixture was filtered by suction, and 8.5 g. of a mixture of sodium chloride and unchanged starting material was collected.

The filtrate was concentrated to a small volume *in vacuo*, the distillate was collected in a receiver at −60°, and the residue dissolved in benzene was chromatographed on a 500-g. Florisil column prepared in petroleum ether. The column was eluted successively with petroleum ether, benzene, ether and methanol.

After most of the solvent had been removed from the petroleum ether fraction, it was combined with the trapped *t*-butyl alcohol and distilled through a vacuum-jacketed Vigreux column at atmospheric pressure to give 6.29 g. (39 mmoles, 30%) of **iodobenzene** whose **infrared** spectrum was identical to that of an authentic sample.

The benzene fraction contained 10.7 g. of a yellow oil, which was crystallized by trituration with ether to yield 7.2 g. of a tan solid. This solid was shown by paper chromatography to be a mixture of three compounds. A small sample of this mixture was recrystallized four times from ether to give a white compound, m.p. 124–125°, identified as ***t*-butyl 2-phenyl-1,3-indandione-2-carboxylate (VII)**. The ultraviolet absorption spectrum of the compound in ethanol showed the bands given as λ_{max} (ϵ_{max}): 229 (55,000), 250 (12,900) and 304 mμ (915).

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.29; H, 5.67.

The ether filtrates from the recrystallizations were concentrated to dryness and triturated with methanol, giving white crystals of **2,2-diphenyl-1,3-indandione** (II). The m.p. after two recrystallizations from ethanol was 118–119°; mixture with an authentic sample did not depress the melting point. The infrared spectrum was identical to that of an authentic sample.

The ether fraction from the chromatographic column yielded 1.9 g. of a white solid, identified as **ethyl 2-phenyl-1,3-indandione-2-carboxylate** (VI) from its infrared and ultraviolet spectra. After four recrystallizations from ether the compound had m.p. 125–126°. The ultraviolet absorption spectrum of the ester in ethanol showed the bands as λ_{max} (ϵ_{max}) at 229 (50,500), 250 (11,800) and 304 mμ (945).

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.71. Found: C, 73.06; H, 4.81.

A sample of the solid mixture isolated from the benzene fraction when chromatographed in a hexane–methyl Carbitol system along with the proper standards showed the three components to be in order of decreasing polarity: ethyl 2-phenyl-1,3-indandione-2-carboxylate, 2,2-diphenyl-1,3-indandione and *t*-butyl 2-phenyl-1,3-indandione-2-carboxylate. This mixture was chromatographed quantitatively in the same system. The three zones were eluted with ethanol, and the concentrations were determined by ultraviolet spectroscopy. From this analysis there were obtained 4.40 g. (13.7 mmoles, 13%) of *t*-butyl 2-phenyl-1,3-indandione-2-carboxylate; 1.6 g. (5.7 mmoles, 6%) of 2,2-diphenyl-1,3-indandione and a total of 3.0 g. (10.2 mmoles, 10%) of ethyl 2-phenyl-1,3-indandione-2-carboxylate. Thus a 29% yield of phenylated products was obtained from this reaction.

In addition to the three phenylated compounds, 5.0 g. of a red solid was isolated from the methanol eluate. This solid did not melt at 300°, left an ash when ignited, showed no iodine on sodium fusion, was soluble in water and alcohols and gave a brown amorphous solid when acidified with dilute hydrochloric acid. From these data and the infrared spectrum, a salt of an unsaturated triketone IV has been proposed.

Hydrolysis of Products from Reaction of the Sodium Salt of Ethyl 1,3-Indandione-2-carboxylate with Diphenyliodonium Chloride.—In one phenylation of the sodium salt of ethyl 1,3-indandione-2-carboxylate (104 mmoles) which after refluxing for three days still contained substantial amounts of starting materials (~30%), no attempt was made to isolate the phenylated products as such. Instead the products were isolated after hydrolysis and decarboxylation. After the reaction was run as described above, the crude benzene and ether fractions from the chromatographic column were combined. The resulting 6.0 g. of yellow oil was suspended in 200 ml. of 3 *N* hydrochloric acid, and enough methanol was added to dissolve the brown gum. The mixture was then heated with stirring near the boiling point for 25 minutes. During this time evolution of carbon dioxide was noted. Most of the methanol was then removed and the mixture was cooled and extracted with methylene chloride. The methylene chloride in turn was extracted thoroughly with 1 *N* sodium hydroxide to remove the acidic component, washed with water and evaporated to dryness. After removal of the solvent, the residue, constituting the neutral fraction, was triturated with ethanol to yield 0.77 g. of yellow prisms of **2,2-diphenyl-1,3-indandione**, m.p. and mixed m.p. after recrystallization from ethanol 122–123°. The infrared spectrum of this compound was identical to that of an authentic sample.

The aqueous sodium hydroxide extract upon acidification with 6 *N* hydrochloric acid yielded 1.07 g. of **2-phenyl-1,3-indandione**, m.p. and mixed m.p., after recrystallization from benzene–petroleum ether, 147–148°. The infrared spectrum was identical to that of an authentic sample.

Determination of Benzene Formed in the Phenylation Reactions.—The phenylations of 2-phenyl-1,3-indandione, 1,3-indandione and the sodium salt of ethyl 1,3-indandione-2-carboxylate were carried out under identical conditions to the ones described above on a 1-gram scale. After the proper reaction time the *t*-butyl alcohol was distilled through a fractionating column and the amount of benzene in the distillate was determined by ultraviolet spectroscopy from the optical density at 254 mμ. The amount of benzene found was 20, 12 and 8%, respectively. It was established by control experiments that the benzene detected in these reactions was not due to the decomposition of the iodobenzene present, but rather arose from intermediates formed during the phenylation (probably phenyl free radicals).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY, STANFORD, CALIFORNIA, THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY, NEW YORK 53, NEW YORK AND THE DEPARTMENT OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF COPENHAGEN, DENMARK]

Inherently Dissymmetric Chromophores and Circular Dichroism

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Ultraviolet circular dichroism (C.D.) curves have been measured for a group of optically active substances possessing inherently dissymmetric chromophores (β,γ-unsaturated ketones and twisted biaryls) and compared with their ultraviolet absorption spectra and optical rotatory dispersion (O.R.D.) curves. The correspondence between these three spectral properties is discussed and confirms the earlier enunciated deductions of the relationship between absolute configuration and optical rotatory power of such inherently dissymmetric chomophores. Circular dichroism has been found particularly useful in this instance for defining the optical rotatory contribution of each individual optically active transition.

The Cotton effect associated with a particular electronic transition manifests itself in two complementary phenomena: *circular dichroism* (C.D.)[4] and *anomalous optical rotatory dispersion* (O.R.D.). For reasons of instrumentation, it is the latter which has received virtually exclusive attention in recent years.[5] However, the same structural information is contained in the measurement of either phenomenon, since the shape of the partial C.D. curve and its signed intensity (a measure of the rotational strength) can be related in a known way to the shape of the associated partial O.R.D. curve and its signed amplitude.[6]

In the case of inherently dissymmetric chromophores,[6,7] the C.D. is particularly interesting. Not only does the sign of the C.D. reflect the chirality of the chromophore, but, subject to certain assumptions, theory also predicts that the partial C.D. curve and partial absorption are proportional, i.e., are of the same shape to within a scale factor.[6,8] The relationship between the absolute configuration and O.R.D. of inherently dissymmetric chromophores (as represented by conjugated and homoconjugated π-systems) has recently been the subject of intensive study.[9] In the present paper we wish to report results bearing on the utility of C.D. in studies of absolute configuration and optical rotatory power of such inherently dissymmetric chromophores.

The β,γ-unsaturated ketones constitute a class of compounds for which the optical rotatory phenomena have been successfully discussed in terms of a twisted composite chromophore formed from carbonyl and olefinic moieties,[10-13] *i.e.*, in terms of an inherently dissymmetric chromophore. The C.D. curves of selected key substances in this group are reported (solid lines) in Fig. 1 (parasantonide, I), Fig. 2 (dehydronorcamphor, II), Fig. 3 (bicyclooctenone, III), and Fig. 4 (dimethyldibenzsuberone, IV (R-configuration) and V (S-configuration) along with the absorption curves (dashed lines). The high rotational strengths of the disymmetric chromophores find expression in the large values of

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[1] In view of the intimate connection between circular dichroism and optical rotatory dispersion, all circular dichroism studies from the Stanford laboratories will be considered part of our series "Optical Rotatory Dispersion Studies." The present paper represents part LXXVI; for part LXXV see, C. Djerassi and W. Klyne, *Proc. Natl. Acad. Sci., U. S.*, **48**, June (1962). The work at Stanford University has been supported by the National Science Foundation (Grant No. G-19905).

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[4] For some examples of previous measurements of circular dichroism see: W. Kuhn and E. Braun, *Z. physik. Chem. (Leipzig)*, (*B*) **8**, 445 (1930); J.-P. Mathieu, *J. chim. phys.*, **33**, 78 (1936); S. Mitchell and K. Schwarzwald, *J. Chem. Soc.*, 889 (1939); and further references cited by W. Kuhn, *Ann. Rev. Phys. Chem.*, **9**, 417 (1958). For more recent studies see J. Badoz, M. Billardon and J.-P. Mathieu, *Compt. rend.*, **251**, 1477 (1960); L. Velluz and M. Legrand, *Angew. Chem.*, **73**, 603 (1961); R. Deen, D.Sc. Thesis, Leiden, 1961.

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