

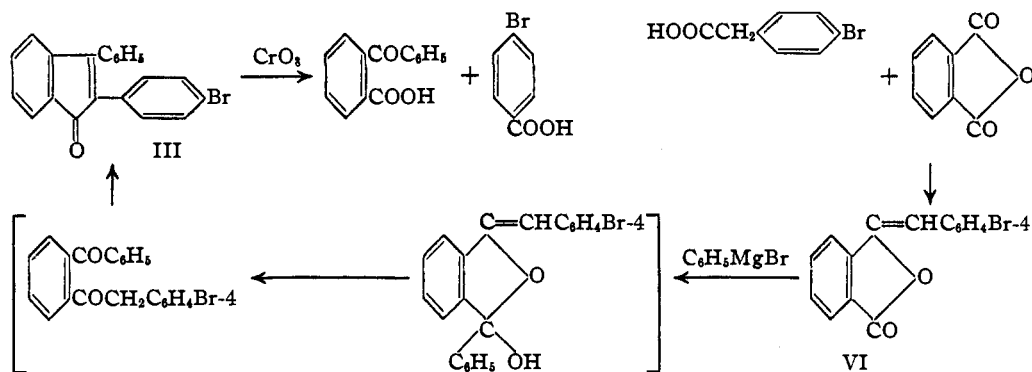
[CONTRIBUTION NO. 898 FROM THE KODAK RESEARCH LABORATORIES]

An Apparently Anomalous Bromination in the Polyphenylindene Series

BY C. F. H. ALLEN AND J. W. GATES, JR.

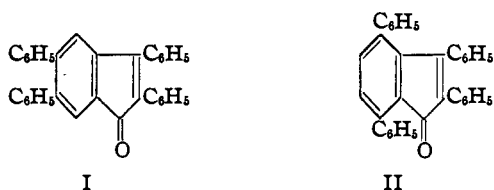
During the investigation of the behavior of certain polyphenylated indenones with bromine,¹ it was observed that 2,3,5,6-tetraphenylindenone I was very slowly brominated in acetic acid solution, with evolution of hydrogen bromide. The rate of this bromination was greatly accelerated

three described by Koelsch.² An oxidative degradation procedure gave *p*-bromobenzoic and *o*-benzoylbenzoic acids; thus, the new substance is 2-(4'-bromophenyl)-3-phenylindenone III. This structure was confirmed by synthesis, as outlined below.



when hydrogen bromide was added to the acetic acid. The formation of a monobromo substitution product was entirely unexpected, for there are no available easily replaceable hydrogen atoms; every hydrogen is present on an aromatic ring.

Only one bromine atom is introduced, even with an excess of the reagent. The bromine is inactive, indicating that it is aromatically bound.

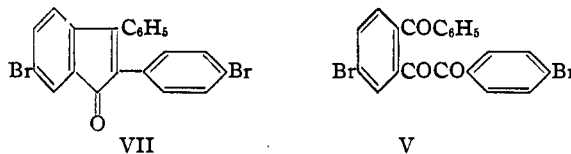


A priori, it was assumed that the bromine had substituted on the Ar ring; that this was incorrect was shown by the formation of a dibromo substitution product from another polyphenylated indenone (II) in which those positions were blocked by phenyl groups. The inevitable conclusion was thus reached that the bromine is on one of the phenyl groups.

With one equivalent of bromine, 2,3-diphenylindenone exhibits a similar behavior. The monobromo derivative is not identical with any of the

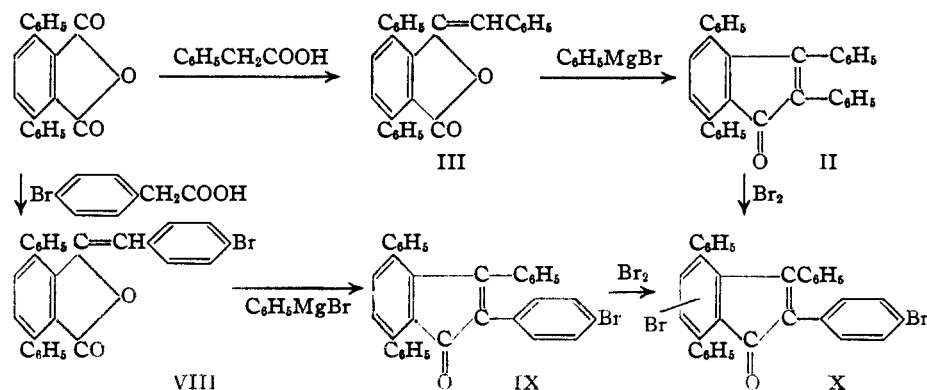
The first bromoindenone was degraded in a similar manner, to *p*-bromobenzoic acid and 4,5-diphenyl-2-benzoylbenzoic acid; therefore, it is 2-(4'-bromophenyl)-3,5,6-triphenylindenone IV.

With an excess of bromine, 2,3-diphenylindenone gave a disubstitution product. Stepwise degradation³ gave the benzil V and then cleavage of this formed *p*-bromobenzoic acid and the known 2-benzoyl-5-bromobenzoic acid.⁴ Hence, in this instance the second bromine atom has entered the aromatic ring of the indenone, and the dibromo derivative has the structure VII.



2,3,4,7-Tetraphenylindenone II gave a mixture of products when brominated, the same technique being used. From the mixture a dibromo substitution product X was isolated. The latter was also secured by a further bromination of a monobromoindenone IX which had been synthesized by an unambiguous method.⁵

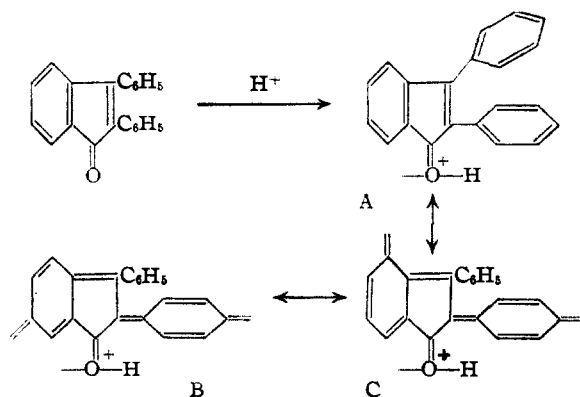
(2) Koelsch, *ibid.*, **58**, 1329 (1936).(3) Allen and Spanagel, *ibid.*, **55**, 3773 (1933).(4) Stephens, *ibid.*, **43**, 1953 (1921).(5) Löwenstein and Ulich, *Ber.*, **58**, 2862 (1925).(1) Allen and Gates, *This Journal*, **64**, 2127 (1942)



The synthesis of IX served to locate one bromine atom in the para position of the 2-phenyl group, and this was confirmed by the oxidative degradation procedure,³ in which *p*-bromobenzoic acid was isolated. Since the dibromoindenone X was formed on further bromination of IX, the position of one of the bromine atoms in X is also known; and as X was obtained during the bromination of II, this reaction furnishes an additional example of the anomalous substitution reaction.

Using the elegant synthesis of Löwenbein and Ulich,⁵ other indenones were synthesized. These included 2,3,5,6-tetraphenylindenone I, previously obtained in the degradation of the bimolecular product resulting from the action of acidic dehydrating agents on anhydracetonebenzil.³ For added confirmation of identity, it was converted into its phenyl carbinol⁶ by the action of phenylmagnesium bromide. The carbinol was identical with a specimen secured from the indenone which had been prepared from anhydracetonebenzil.

Since the bromination of the polyphenylindenones occurs only in the presence of hydrogen bromide, it would seem that the first step is the addition of a proton to the oxygen atom, resulting



(6) Allen and Gates, *THIS JOURNAL*, **64**, 2125 (1942).

in a charged molecule A. Now, such a molecule can be assumed to be a hybrid of several contributing structures, of which B and C may be mentioned specifically.

It may well be that such quinonoid bond structures are favored in a charged molecule. It would account for the lack of bromination on the 3-phenyl group. Phenyl groups on the Ar ring may block the entrance of a bromine atom, as in I. If the interpretation has merit, it should be possible to introduce an atom of bromine in the 6-position, by virtue of the resonance form B. Such a substance was found in the 2-(4'-bromophenyl)-3-phenyl-6-bromoindenone VII. The unlocated bromine atom in X is also probably in the 6-position.

One superficially similar case was recently described in the literature⁷ in which 4'-bromophenylfurans were unexpectedly obtained in the treatment of certain arylolethylenes with hydrogen bromide. The authors showed that bromine was formed during the reaction, by the use of β -naphthol to remove it as formed; consequently, this bromofuran must have been a result of direct bromination of the furans. In line with this conclusion, a dibromofuran was obtained when there were two available phenyl groups.

Experimental

The necessary anhydrides^{8,9,10} were prepared as directed in the literature, except that 3,4,5,6-tetraphenylphthalic acid,¹¹ heated just before use, was employed. *p*-Bromophenylacetic acid was secured by the hydrolysis of *p*-bromobenzyl cyanide.¹²

(7) Couper and Lutz, *J. Org. Chem.*, **7**, 79 (1942).

(8) 3,6-Diphenyl: Weizmann, Bergmann and Haskelberg, *J. Chem. Soc.*, 394 (1939).

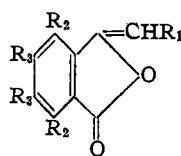
(9) 4,5-Diphenyl: Allen, Eliot and Bell, *Can. J. Research*, **17**, 86 (1939).

(10) 3,6-Dimethyl-4,5-diphenyl: Allen and VanAllan, *THIS JOURNAL*, **64**, 1266 (1942).

(11) Allen and Sheps, *Can. J. Research*, **11**, 171 (1934).

(12) Dippy and Williams, *J. Chem. Soc.*, 164 (1934).

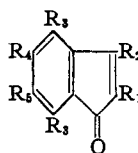
TABLE I
PROPERTIES OF BENZALPHTHALIDES



No.	R ₁	R ₂	R ₃	M. p., °C.	Empirical formula	Analyses, %					
						Calcd.		Found		Found	
						C	H	Br	C	H	Br
VI	C ₆ H ₄ Br-4	H	H	154-155	C ₁₅ H ₉ O ₂ Br			26.6			
	C ₆ H ₅	C ₆ H ₅	H	166-167	C ₂₇ H ₁₈ O ₂	86.6	4.9		86.1	4.8	
VIII	C ₆ H ₄ Br-4	C ₆ H ₅	H	213-214	C ₂₇ H ₁₇ O ₂ Br			17.7			17.7
"	C ₆ H ₅	CH ₃	C ₆ H ₅	232-233	C ₂₉ H ₂₂ O ₂	86.6	5.5		86.3	5.8	
	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	338-340	C ₃₉ H ₂₆ O ₂	89.0	5.0		88.7	4.8	
	C ₆ H ₅	H	C ₆ H ₅	212-213	C ₂₇ H ₁₈ O ₂	86.6	4.9		86.6	5.1	

^a Also obtained from the dihydroanhydride, the two hydrogen atoms being lost during the reactions above 290°.

TABLE II
PROPERTIES OF POLYPHENYLINDENONES



No.	R ₁	R ₂	R ₃	R ₄	R ₅	M. p., °C.	Empirical formula	Analyses, %					
								Calcd.		Found		Found	
								C	H	Br	C	H	Br
	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	279-280	C ₁₆ H ₁₀ O	92.2	5.1		92.0	5.2	
III	C ₆ H ₄ Br-4	C ₆ H ₅	H	H	H	145-146	C ₂₁ H ₁₃ OBr			22.2			22.3
IX	C ₆ H ₄ Br-4	C ₆ H ₅	C ₆ H ₅	H	H	257-258	C ₃₃ H ₂₁ OBr			15.6			15.2
II	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	H	H	204-205	C ₃₃ H ₂₂ O	91.2	5.1		91.5	5.0	
	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	CH ₃	C ₆ H ₅	234-235	C ₃₅ H ₂₆ O	90.9	5.6		90.7	6.0	
VII	C ₆ H ₄ Br-4	C ₆ H ₅	H	H	Br	201-202	C ₂₁ H ₁₂ OBr ₂			36.4			36.3
X	C ₆ H ₄ Br-4	C ₆ H ₅	C ₆ H ₅	H	Br	254-255	C ₃₃ H ₂₀ OBr ₂			27.0			27.3
IV	C ₆ H ₄ Br-4	C ₆ H ₅	H	C ₆ H ₅	C ₆ H ₅	200-201	C ₃₃ H ₂₁ OBr			15.6			15.6

The benzalphthalides were all obtained by following the procedure described for benzalphthalide itself.¹³ Their properties are collected in Table I.

The polyphenylindenones were obtained by treatment of the various benzalphthalides with the appropriate Grignard reagents by the standard procedure⁸; the yields were 60-70%. Their properties are collected in Table II.

Bromination.—This is best illustrated by an example. To a solution of 7 g. of 2,3-diphenylindenone in 50 cc. of glacial acetic acid was added first 4.4 g. of bromine in 10 cc. of the same solvent and then 1 cc. of a 30-32% solution of hydrogen bromide in acetic acid, and the mixture heated for four hours on the steam-bath. The product that crystallized upon being cooled was filtered and purified by appropriate manipulation. The yield was 5 g., and the melting point (145-146°) was not depressed on admixture with an authentic specimen of III.

The other brominations were done in a similar manner, but the time of heating was doubled. Their properties are included in Table II. The dibromodiphenylindenone VII was formed by direct bromination of 2,3-diphenylindenone, and also by further bromination of the monobromo derivative III. From the mixed bromination product of II were isolated various fractions all melting in the same range, but containing varying amounts of bromine approximating the composition of a monobromo substitution product. Upon oxidation, a mixture of benzoic acid and *p*-bromobenzoic

acid resulted. It seems, therefore, that this is a mixture and not a definite monobromoindenone.

It should be pointed out that hydrogen bromide by itself has no action on the polyphenylated indenone.

Oxidation (a) by Chromium Trioxide.—This was carried on by the customary procedure, and the mixture of acid separated by crystallization. Identification was by mixed melting points with authentic specimens in every instance. The dibromoindenone VII gave *p*-bromobenzoic and 5-bromo-2-benzoylbenzoic acids; the monobromoindenone IV gave *p*-bromobenzoic and 4,5-diphenyl-2-benzoylbenzoic acids, m. p. 240-241°.¹⁴

(b) by **Permanganate in Acetone.**—This was carried out in only one instance, that of III. It gave 4',5'-dibromo-2-benzoylbenzil V, m. p. 140-141°.

Anal. Calcd. for C₂₁H₁₂O₃Br₂: Br, 33.9. Found: Br, 33.9.

This benzil was cleaved by alkaline hydrogen peroxide to *p*-bromobenzoic and 5-bromo-2-benzoylbenzoic acids.

The authors gratefully acknowledge the helpful suggestions of Dr. A. Weissberger.

Summary

Polyphenylated indenones are brominated in the presence of hydrogen bromide.

When there are phenyl groups in the 2,3,5- and

(13) *Org. Syn.*, **13**, 10 (1933).

(14) Allen, Bell and VanAllan, *THIS JOURNAL*, **62**, 662 (1940).

6-positions, one bromine only enters the molecule. This bromine atom appears in the para position of the 2-phenyl group.

With 2,3-diphenylindenone, one or two bromine atoms can be introduced. The first one also enters the para position of the 2-phenyl group. The second takes the 6-position of the indene ring system.

Similarly, with 2,3,4,7-tetraphenylindenone, one

bromine atom appears in the para position of the 2-phenyl group.

A mechanism has been proposed to account for these unexpected results.

2,3,5,6-Tetraphenylindenone, the first step in the degradation of the bimolecular product formed by the action of acidic dehydrating agents upon anhydracetonebenzil, has been synthesized.

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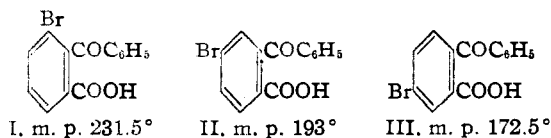
Indanone Ring Closure of Unsymmetrical β,β -Diarylpropionic Acids

BY C. F. H. ALLEN AND J. W. GATES, JR.

Thirty years ago it was shown¹ that in the Friedel-Crafts reaction, unsaturated acid chlorides gave a variety of products, among which were ketones in the indane series. Cyclic bromo ketones were also obtained with the dihalo acid chlorides. The evidence for the structure of the bromoindanones, so formed, was based upon the nature of the products secured by permanganate oxidation of one of them, but the position of the bromine atom in the oxidation product (a bromobenzoylbenzoic acid) was not determined except by inference from the nature of the starting material and supposed course of the reaction—assumptions that seemed valid and sufficient at that time.

Ten years later, others had occasion to utilize the reaction, but did not secure any of the indanones.²

In a study of the behavior of the bromophthalic anhydrides and benzene in the presence of anhydrous aluminum chloride, Stephens³ obtained three bromobenzoylbenzoic acids, I, II, III, and proved the structures of II and III. The structure assigned to I was in error, but this has been recently corrected.^{3a}

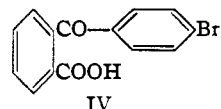


In speaking of the isomer III, Stephens says, "This substance is, no doubt, identical with the one described by Kohler, Heritage and Burnley (m. p. 174°). . . ."

- (1) Kohler, Heritage and Burnley, *Am. Chem. J.*, **44**, 60 (1910).
- (2) McKenzie and Barrow, *J. Chem. Soc.*, **119**, 72 (1921).
- (3) Stephens, *THIS JOURNAL*, **43**, 1950 (1921).
- (3a) Huntress, Pfister and Pfister, *ibid.*, **64**, 2846 (1942).

Waldmann⁴ obtained but one acid, m. p. 191°, by the same procedure used by Stephens, and by an independent method showed it had the structure II as assigned by Stephens. He assumed that Kohler's acid, m. p. 174°, was impure or had the structure III, and "corrected" the structure of the bromoindanone from which it had been made. The acid, m. p. 192°, has also been obtained as an oxidation product of a bromodiphenylindenone.⁵

The isomeric 4'-bromobenzoylbenzoic acid IV, apparently overlooked by the various authors, also has a melting point of 173°.⁶



During an investigation of an apparently anomalous bromination in the polyphenylated indenone series,⁷ several discrepancies between the properties of some of our products and those described in the literature were found. In order to clear up the uncertainty, it became necessary to try to repeat enough of the earlier work to secure specimens for comparison and for mixed melting point determinations.

In agreement with McKenzie, but contrary to Kohler, we were unable to obtain the cyclic bromoindanone by the use of anhydrous aluminum chloride with the cinnamoyl chlorides and bromobenzene; in each instance a saturated propionic acid which could be converted to the desired indanone by formation of its acid chloride, followed

- (4) Waldmann and Mathiowetz, *J. prakt. Chem.*, **126**, 69 (1930).
- (5) Koelsch, *THIS JOURNAL*, **58**, 1330 (1936).
- (6) Ullmann and Sone, *Ann.*, **380**, 337 (1911).
- (7) Allen and Gates, *THIS JOURNAL*, **65**, 419 (1943).