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2-Arylindane-1,3-diones—A New Class of Radical-active Compounds

V.V.Moiseev and I.T.Poluktov

Being cyclic β-diketones, 2-arylindane-1,3-diones play an active part in radical reactions: they react vigorously with stable radicals, inhibit the autoxidation of hydrocarbons and polymers, accelerate radical polymerisation, are effective chain-transfer agents in polymerisation, and are oxidised by oxygen and inorganic oxidants. In several radical reactions they behave like phenols, and are more reactive than the latter. A list of 141 references is included.

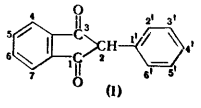
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I. INTRODUCTION

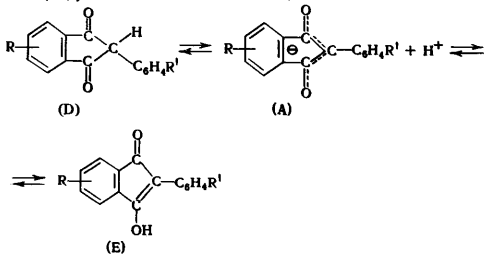
Phenols, amines, thiols, sulphides, and phosphorus-containing compounds are the main classes of organic compounds which actively influence radical reactions. They are widely used as inhibitors of the autoxidation of organic compounds in the liquid phase, stabilisers for polymers, regulators of polymerisation, and inhibitors of radical polymerisation[1-6].

During recent years a new class of radical-active compounds, 2-arylindane-1,3-diones, has been attracting the interest of research workers. The best known representative of this type is 2-phenylindane-1,3-dione



(I)

which was first synthesised in 1893 by Nathanson[7]. In the past a great deal of work was done on the preparation of its derivatives. The synthesis of 2-arylindane-1,3-diones is quite simple and can be accomplished by several methods[8-15]. All known 2-arylindane-1,3-diones are crystalline compounds, several of which are coloured[16]. They can exist in three forms[17]—in the diketo-form (D), as an anion (A), and as an enol (E):



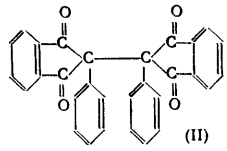
(D) (A) (E)

Equilibrium is established between these forms depending on the nature of substituents, the pH of the solution, and the medium, which makes 2-arylindane-1,3-diones extremely useful subjects for investigation from many points of view. Work on the preparation of substituted derivatives was stimulated by their practical application as blood anticoagulants. 2-Phenylindane-1,3-dione has been used in medical practice under the name "Fenilin".[10]

Although the first radical reactions were observed long ago by Nathanson, study of the oxidation of 2-phenylindane-1,3-dione by oxides of nitrogen and other oxidants was only the beginning of the investigation of these reactions as applied to 2-arylindane-1,3-diones. The need to study the behaviour of these compounds in radical reactions has arisen[18] as part of the problem of the interrelationship of structure, reactivity in homolytic reactions, and physiological activity in a series of indane-1,3-dione derivatives. Although the latter two relations could not be established[19,20], examination of the radical reactions of 2-arylindane-1,3-diones was of intrinsic practical and theoretical interest. The first systematic investigation[21] and subsequent work together with researches by other investigators have shown that these are radical-active compounds with a wide range of action. They react vigorously with stable radicals, inhibit liquid-phase oxidations, and stabilise polymers. They have a peculiar influence on radical polymerisation, acting as accelerators and regulators. In several cases 2-arylindane-1,3-diones are more effective than known compounds of other classes in their reactivity.

II. OXIDATION OF 2-ARYLINDANE-1,3-DIONES BY OXYGEN

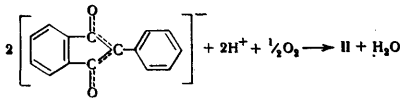
2-Arylindane-1,3-diones are quite easily oxidised by oxygen. The prolonged boiling[22] of an alcoholic solution of 5-methyl-2-phenylindane-1,3-dione in air produces dimerisation. In sodium hydrogen carbonate solution 2-phenylindane-1,3-dione is converted into the dimer—1,2-diphenyl-1,2-diphthaloylethane



(II)

in six weeks; an alcoholic solution of the diketone is decolorised in three weeks[23]. Methanolic solutions of 2-arylindane-1,3-diones are more stable than aqueous solutions[24]. Sodium 1,3-dioxo-2-phenylindane-4-sulphonate(III) is the least stable among these compounds: aqueous solutions of concentration 10^{-4} M at pH 4.3, 10^{-3} M,

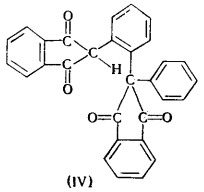
and 10^{-2} M undergo 50%, 30%, and 5% decomposition respectively in 1 h. The rate of oxidation of (III) depends on pH: the compound is most stable at pH 0, the rate of oxidation increasing with change in hydrogen-ion concentration in either direction. In strongly alkaline media, containing few hydrogen ions, a 0.001 M solution of (III) is almost unchanged after 1 h. The part played by hydrogen ions in the conversion of sodium 1,3-dioxo-2-phenylindane-4-sulphonate is indicated by the considerable rise in pH observed during the oxidation. It is suggested that the oxidation of 2-phenylindane-1,3-dione to a dimer takes place via a conjugated anion:



A kinetic study by Sztark[25] has shown that the oxidation of 2-phenylindane-1,3-dione in aqueous solution is a first-order reaction with a rate of 2.45×10^{-4} h^{-1} at 20°C and pH 12. The activation energy is 6.164×10^{-4} J $mole^{-1}$ deg^{-1}. The mean temperature coefficient of the reaction is 1.7. The extrapolated half-decomposition time at 20°C is 164 days.

Fig. 1 shows the pH dependence of the rate of oxidation of 2-phenylindane-1,3-dione. The diketone is seen to be most stable at pH 9.

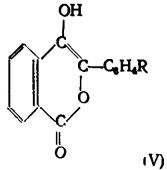
The oxidation of 2-arylindane-1,3-diones by oxygen can occur in two ways—with the formation of dimers as above and of 4-hydroxyisochroman-1-ones[26,27], which are then converted into acids and derivatives of benzoylphthalide. The dimer (II) is always formed when 2-phenylindane-1,3-dione is oxidised in alcohol, in ether, and also in pyridine in the presence of copper(I) bromide[28,29]. In this case oxidation is rapid, and together with (II) a small quantity of an isomeric dimer



(IV)

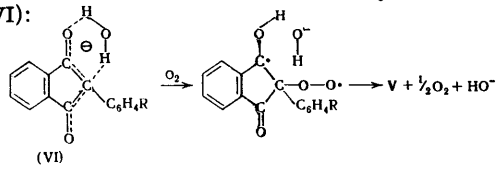
2-phenyl-*o*-phenylenebis-2,2′-indane-1,3-dione, is also isolated. The structure and the reactions of the dimer (II) have been studied quite fully[30-33]. 2-*p*-Methoxyphenylindane-1,3-dione in toluene at room temperature is easily dimerised by the action of oxygen[34]; oxidation of 2-*p*-dimethylaminophenylindane-1,3-dione has been observed during synthesis[35].

In an alkaline medium at 60–80°C 2-arylindane-1,3-diones are converted into substituted isocoumarins[27,36-39]



(V)

It has been suggested[38] that the conversion in alkaline aqueous solution involves oxidation of a hydrated diketone anion (VI):



(VI)

The addition of copper salts to an alkaline solution of 2-phenylindane-1,3-dione not only accelerates oxidation but also changes the composition of the products[27]: both 4-hydroxy-3-phenylisochroman-1-one and the dimer (II) are formed. The quantity of dimer increases with increase in the concentration of copper ions. The formation of various acids in the oxidation of 2-phenylindanedione is probably due to further oxidation and conversion of the 3-phenyl derivative (V) in alkaline medium, although this is a matter of controversy[40]. Substituted 4-hydroxy-3-phenylisochroman-1-ones are formed also when 2-arylindanediones undergo oxidation in the presence of amines[34,41]. The oxidation of diketones is accelerated by amines. Vanag and Pilegis[42] noted the formation of complexes of 2-phenylindanedione with amines.

Ozolina and Neilands[43-46] observed the oxidation by atmospheric oxygen of biphenyl and diphenyl oxide analogues of 2-arylindanediones.

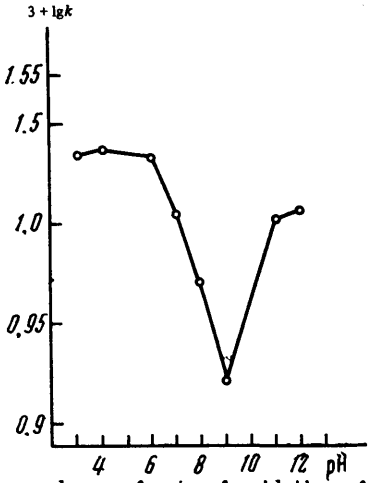


Figure 1. Dependence of rate of oxidation of 2-phenylindanedione on pH of solution.

III. ACTION OF INORGANIC OXIDANTS

In 1893 Nathanson[7] first obtained 1,2-diphenyl-1,2-diphthaloylethane (II) by passing oxides of nitrogen into an alcoholic solution of 2-phenylindane-1,3-dione. The action of pentyl nitrite produced a similar result. Boiling an alcoholic solution of 2-phenylindanedione with sodium nitrite became a simple and convenient method[7,21,23] for obtaining the dimer (II) as well as dimers[22] from substituted 2-phenylindanediones.

Formation of dimers is observed also when substituted indane-1,3-diones are treated with other oxidants. Nitric acid[47] oxidises 2-*m*-tolylindanedione; the dilute acid causes[48,49] dimerisation of the 2-*p*-nitrophenyl and 2-*p*-methoxyphenyl compounds. The nitration of 4,5-dimethoxyindane-1,3-dione produces as byproduct[50] a dimer of 4,5-dimethoxy-2-nitroindanedione. 2-Arylindanediones are easily oxidised by iodine[33,51,52] and by potassium hexacyanoferrate(III)[22,51] in an alkaline medium:

$$\Phi^- + Fe(CN)_6^{3-} \rightarrow \Phi^{\cdot} + Fe(CN)_6^{4-}$$

$$2\,\Phi^{\cdot} \rightarrow \Phi{-}\Phi$$

where Φ^- is the anion of 2-phenylindane-1,3-dione.

2-Methylindane-1,3-dione is oxidised to a dimer by potassium persulphate[53,54]. Substituted 2-phenylindanediones are oxidised to the corresponding dimers by potassium hexacyanoferrate(III), ammonium persulphate, and iron(III) chloride[55,56]. Ethyl 1,3-dioxoindanecarboxylate dimerises under the influence of lead dioxide[57]. Dimers are formed from 2-arylindanediones also in other reactions—in the thiocyanation[58] of the 2-halogeno-derivatives, in the interaction[59,60] of 2-bromo-2-*p*-nitrophenylindanedione with various amines, on treatment[61] of 2-bromo-2-phenylindanedione with alcoholic ammonia and with copper powder, and also on interaction with sodium 2-phenylindanedione. Dimers are formed also[62,63] when 2-aryl-2-iodoindanediones are heated and when 2-nitro-2-*p*-nitrophenylindanedione is boiled in anhydrous carbon tetrachloride or acetic acid[27]. Heating 2-bromo-5-methyl-2-phenylin-

anode both in alkaline[73-77] and in acid[77-82] media. Current–voltage measurements with a controlled current have been successfully applied to the anodic oxidation of β-diketones. In an alkaline medium the 2-arylindanedione anion undergoes oxidation; but in an acid medium the anodic current is maintained by oxidation of the enolic form[82]. In both cases the oxidation products are assumed to be the corresponding dimers. Table 1 lists the oxidation potentials relative to the saturated calomel electrode of the anions $E^{A}_{1/2}$[74] and of the undissociated enolic forms $E^{E}_{1/2}$[80] of substituted 2-phenylindanediones. These results clearly show the influence of substituents on the ease of electrochemical oxidation: electron-donating substituents considerably facilitate oxidation; the effect of substituents in the phthaloyl fragment[77] is considerably more complicated.

atom, activation energies E, and pre-exponential factors k_0 for reaction of the radical with the above compounds in dioxan at 20°C. The activation energy could not be determined for 2-naphth-2′-ylindane-1,3-dione, since it is obviously very small. The values found for the rate constants and activation energies for the 2-arylindanediones are close to those for the corresponding reaction of DPPH with phenols[99-101].

Table 2. Rate constants for the reactions of diphenylpicrylhydrazyl with 2-arylindanediones.

Aryl	a	k_1, M^{-1} min^{-1}	E, kcal $mole^{-1}$	k_0, M^{-1} min^{-1}
Phenyl	1.9	$7.9 \cdot 10^2$	5.5	$1.0 \cdot 10^7$
p-Chlorophenyl	1.7	$16.8 \cdot 10^2$	2.8	$2.0 \cdot 10^6$
p-Bromophenyl	1.7	$17.2 \cdot 10^2$	—	—
Naphth-1′-yl	1.6	$0.41 \cdot 10^2$	7.5	$1.6 \cdot 10^7$
Naphth-2′-yl	1.4	$40 \cdot 10^2$	—	—

The reason for the sharp decrease in reactivity of 2-naphth-1′-ylindanedione (XIX) is the same as in *ortho*-substituted 2-phenylindanediones (XVI and XVII). The nuclear magnetic resonance spectra show[65] that in 2-mesitylindanedione (XVI) the plane of the mesityl ring is perpendicular to that of the indanedione ring, and rotation of the former ring is retarded. The appearance of additional electronic effects in 2-arylindanediones on *ortho*-substitution is confirmed by the ultraviolet spectra[102] and by a change in acidity[17]. Thus the introduction of an *ortho*-substituent disturbs the configuration of the molecule, which leads to a change in mobility of the 2-hydrogen atom in the indanedione ring.

The difference in properties between 1- and 2-substituted naphthalene derivatives attracted attention long ago[103-105] and has been termed an "edge" effect[103], *peri*-interaction[105]. In the field of β-diketones it has been noted that iodo-derivatives[63] of 2-naphth-2′-ylindanedione are thermally less stable than the corresponding naphth-1′-yl derivatives. The construction of Stuart–Briegleb models of compounds (I), (XVI), (XVII), (XIX), and (XX) confirms that, in the *ortho*-substituted derivatives and also in (XIX), the molecular configuration is disrupted by interaction of the substituent and the carbonyl group; the aryl radical in these compounds is unable to rotate freely as in (I) and (XX).

Heating 2-phenylindane-1,3-dione with benzoyl peroxide

constants K determined for azoisobutyronitrile by means of 2-phenylindanedione, and also the initiator efficiencies β in toluene and chlorobenzene at 80°C, show complete agreement with values[109] obtained by other methods. It is interesting that unlike known inhibitors—phenols and amines—the stoichiometric coefficient of inhibition for 2-phenylindanedione is in this case unity. Thus the use of 2-arylindanediones to estimate radicals has certain advantages over such inhibitors as 1-naphthylamine and 1-naphthol in view of the simplicity of quantitative control and the definiteness of the conversion products of the inhibitor. Quantitative determination of 2-phenylindanedione and its analogues can be accomplished also spectrophotometrically[110-114], polarographically[115], bromatometrically[116], by anodic volt–amperometric measurements[76], potentiometrically[117], and by other methods[72].

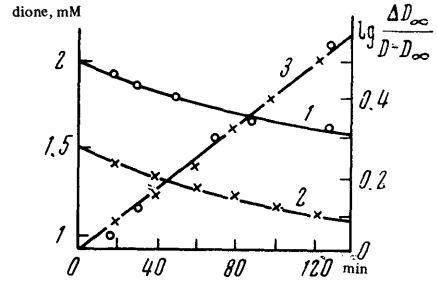


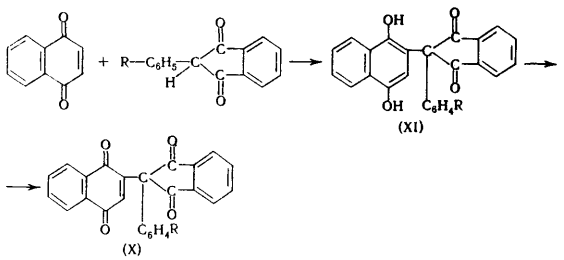
Figure 2. Consumption of 2-phenylindanedione and variation of $\lg [\Delta D_\infty/(D - D_\infty)]$ with time in experiments on the decomposition of azoisobutyronitrile (0.0005 M) in toluene at 80°C: 1), 2) rate curves; 3) optical density.

VI. 2-ARYLINDANE-1,3-DIONES AS OXIDATION INHIBITORS IN THE LIQUID PHASE

The reaction with radicals such as 2,2-diphenyl-1-picrylhydrazyl suggested that 2-arylindane-1,3-diones would retard the oxidation of alkylarenes by oxygen. An inhibiting effect was shown[118] in the oxidation of *p*-di-isopropylbenzene at 100°C: in the presence of 0.06 mole % of 2-phenylindanedione oxidation was delayed for 25 h.

With substituted indane-1,3-diones the reaction may also go differently: thus the interaction of 2-methylsulphonylindanedione with the quinone involves cross recombination of the 1,3-dioxoindanyl radical and of the semiquinone to form 2-(2,3-dichloro-5,6-dicyano-4-hydroxyphenoxy)-2-methylsulphonylindane-1,3-dione.

2-Arylindane-1,3-diones react with 1,4-naphthaquinone[89] in aqueous acetone solution in the presence of an acetate buffer to form a 2-(2-aryl-1,3-dioxoindan-2-yl)naphthaquinone (X), presumably[89] by the oxidation of the intermediate naphthaquinol (XI) by atmospheric oxygen:



(XI)

(X)

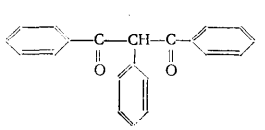
In this case dimers were not isolated. The Reviewers hold a different opinion on the course of the reaction: the first stage is 1,4-addition, the product (XI) is oxidised by the initial 1,4-naphthaquinone, and air oxidises 1,4-naphthaquinol, so that the mechanism is similar to that between quinones and aniline[90].

The redox potential of 1,4-naphthaquinone is 0.484 V, whereas those of benzoquinone and of its 2,3-dichloro-5,6-dicyano-derivative are 0.712 and 1.0 V respectively.

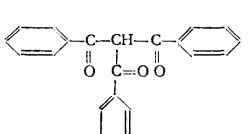
Indane-1,3-dione itself reacts with phenanthraquinone[91] and with nitrophenanthraquinones[92,93] to form 9,9-bis-(1,3-dioxoindan-2-yl)-9,10-dihydro-10-oxophenanthrene and the corresponding nitro-derivative respectively.

V. INTERACTION WITH STABLE RADICALS

The great reactivity of 2-arylindane-1,3-diones towards stable radicals was first observed by Zalukaev and Moiseev[94] in the reaction of diketones with 2,2-diphenyl-1-picrylhydrazyl (DPPH), 2-*p*-methoxyphenyl-2-phenyl-1-picrylhydrazyl[95,96], and 2-*p*-bromophenyl-2-phenyl-1-picrylhydrazyl[21]. With equimolecular proportions of the reactants and an initial concentration of 0.00025 M in toluene at 20°C, the reaction between 2-phenylindanedione and DPPH takes 15–20 s. The reaction of *meta*- and *para*-substituted 2-phenylindanediones with DPPH is equally rapid. This radical detaches the 2-hydrogen atom from the indane ring, as is confirmed by the absence of reaction with 2-methyl-2-phenylindanedione, which does not contain hydrogen in the dione ring. Adding lead dioxide to the 2-arylindanedione system after completion of the reaction regenerates the DPPH radical. Phenyldibenzoylmethane (XII) and tribenzoylmethane (XIII), unlike 2-arylindanediones, do not react with DPPH.

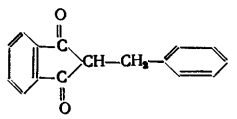


(XII)

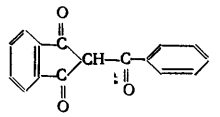


(XIII)

2-Benzyl- and 2-benzoyl-indane-1,3-diones (XIV and XV), in which the dioxoindanyl and phenyl groups are separated by a bridge

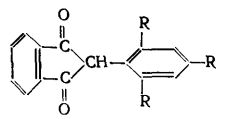


(XIV)



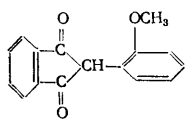
(XV)

also do not react with DPPH under similar conditions. Such diminished reactivity in (XIV) is entirely explicable, since conjugation is considerably weakened by the methylene group[97]. Introduction of an *ortho*-substituent into the phenyl ring produces a sharp decrease in reactivity. No compound of the type

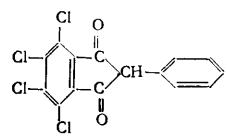


(XVI)
(R=OCH_3, CH_3, C_2H_5, C_3H_7, Br)

reacts either with DPPH or with 2-*p*-methoxyphenyl-2-phenyl-1-picrylhydrazyl in dioxan at 20°C. Even 2-*o*-methoxyphenylindanedione (XVII), which contains one *ortho*-substituent, does not interact with the latter radical. Nevertheless, 4,5,6,7-tetrachloro-2-phenylindanedione (XVIII), which is substituted in the benzene ring of the indanedione system, is highly reactive.

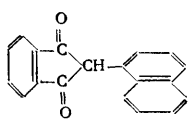


(XVII)

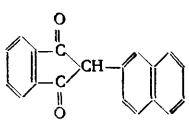


(XVIII)

In order to study the *ortho*-effect[98] a more detailed investigation was made of the reactivity of various substituted indane-1,3-diones—the 2-phenyl (I), 2-*p*-chlorophenyl, 2-*p*-bromophenyl, 2-naphth-1'-yl (XIX), and 2-naphth-2'-yl (XX) derivatives



(XIX)



(XX)

The interaction between 2-arylindanediones and DPPH is a consecutive-parallel reaction:

$$\Phi H + DPPH \xrightarrow{k_1} \Phi\cdot + DPPH - H$$
$$\Phi\cdot + DPPH \xrightarrow{k_2} DPPH - \Phi$$
$$\Phi\cdot + \Phi\cdot \xrightarrow{k_3} \Phi - \Phi$$

Since k_2, $k_3 \gg k_1$, the rate of consumption of DPPH, and hence the rate of detachment of the hydrogen atom from the diketones, are determined by the equation

$$-\frac{d[DPPH]}{dt} = \alpha k_1 [\Phi H][DPPH]$$

where α is the stoichiometric coefficient—the number of radicals that react with one molecule of the dione. The reaction of 2-arylindanediones with DPPH obeys a second-order equation. Table 2 lists the stoichiometric coefficients, the rate constants k_1 of detachment of a hydrogen

atom, activation energies E, and pre-exponential factors k_0 for reaction of the radical with the above compounds in dioxan at 20°C. The activation energy could not be determined for 2-naphth-2'-ylindane-1,3-dione, since it is obviously very small. The values found for the rate constants and activation energies for the 2-arylindanediones are close to those for the corresponding reaction of DPPH with phenols[99-101].

Table 2. Rate constants for the reactions of diphenylpicrylhydrazyl with 2-arylindanediones.

Aryl	a	k_1, M^{-1} min^{-1}	E, kcal $mole^{-1}$	k_0, M^{-1} min^{-1}
Phenyl	1.9	$7.9 \cdot 10^2$	5.5	$1.0 \cdot 10^7$
p-Chlorophenyl	1.7	$16.8 \cdot 10^2$	2.8	$2.0 \cdot 10^5$
p-Bromophenyl	1.7	$17.2 \cdot 10^2$	—	—
Naphth-1'-yl	1.6	$0.41 \cdot 10^2$	7.5	$1.6 \cdot 10^7$
Naphth-2'-yl	1.4	$40 \cdot 10^2$	—	—

The reason for the sharp decrease in reactivity of 2-naphth-1'-ylindanedione (XIX) is the same as in *ortho*-substituted 2-phenylindanediones (XVI and XVII). The nuclear magnetic resonance spectra show[65] that in 2-mesitylindanedione (XVI) the plane of the mesityl ring is perpendicular to that of the indanedione ring, and rotation of the former ring is retarded. The appearance of additional electronic effects in 2-arylindanediones on *ortho*-substitution is confirmed by the ultraviolet spectra[102] and by a change in acidity[17]. Thus the introduction of an *ortho*-substituent disturbs the configuration of the molecule, which leads to a change in mobility of the 2-hydrogen atom in the indanedione ring.

The difference in properties between 1- and 2-substituted naphthalene derivatives attracted attention long ago[103-105] and has been termed an "edge" effect[103], *peri*-interaction[105]. In the field of β-diketones it has been noted that iodo-derivatives[63] of 2-naphth-2'-ylindanedione are thermally less stable than the corresponding naphth-1'-yl derivatives. The construction of Stuart–Briegleb models of compounds (I), (XVI), (XVII), (XIX), and (XX) confirms that, in the *ortho*-substituted derivatives and also in (XIX), the molecular configuration is disrupted by interaction of the substituent and the carbonyl group; the aryl radical in these compounds is unable to rotate freely as in (I) and (XX).

Heating 2-phenylindane-1,3-dione with benzoyl peroxide gives the dimer (II), which is obtained also by interaction of the compound with peroxy-radicals formed on the decomposition of azoisobutyronitrile in the presence of oxygen[21]. The ease with which 2-phenylindanedione can be determined colorimetrically in hydrocarbons[106] has enabled it to be tested in the method of inhibitors. The initiator chosen was azoisobutyronitrile, whose decomposition has been thoroughly studied by various methods[107], including the inhibitor method[108]. Fig. 2 illustrates rate curves for the consumption of 2-phenylindanedione at different concentrations in the presence of azoisobutyronitrile in toluene at 80°C and also the time variation of $\lg [\Delta D\infty/(D - D\infty)]$, where D is the optical density of a sample of the reaction mixture withdrawn during the reaction.

Preliminary results showed that, in chlorobenzene under these conditions, 2-phenylindane-1,3-dione is not consumed by reaction with oxygen. The decomposition constants K determined for azoisobutyronitrile by means of 2-phenylindanedione, and also the initiator efficiencies β in toluene and chlorobenzene at 80°C, show complete agreement with values[109] obtained by other methods. It is interesting that unlike known inhibitors—phenols and amines—the stoichiometric coefficient of inhibition for 2-phenylindanedione is in this case unity. Thus the use of 2-arylindanediones to estimate radicals has certain advantages over such inhibitors as 1-naphthylamine and 1-naphthol in view of the simplicity of quantitative control and the definiteness of the conversion products of the inhibitor. Quantitative determination of 2-phenylindanedione and its analogues can be accomplished also spectrophotometrically[110-114], polarographically[115], bromatometrically[116], by anodic volt-amperometric measurements[76], potentiometrically[117], and by other methods[72].

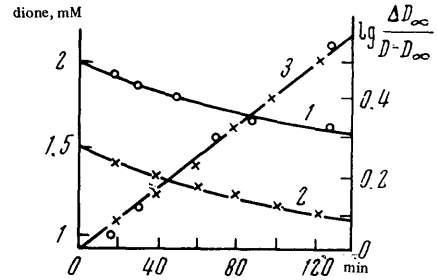


Figure 2. Consumption of 2-phenylindanedione and variation of $\lg [\Delta D\infty/(D - D\infty)]$ with time in experiments on the decomposition of azoisobutyronitrile (0.0005 M) in toluene at 80°C: 1), 2) rate curves; 3) optical density.

VI. 2-ARYLINDANE-1,3-DIONES AS OXIDATION INHIBITORS IN THE LIQUID PHASE

The reaction with radicals such as 2,2-diphenyl-1-picrylhydrazyl suggested that 2-arylindane-1,3-diones would retard the oxidation of alkylarenes by oxygen. An inhibiting effect was shown[118] in the oxidation of *p*-di-isopropylbenzene at 100°C: in the presence of 0.06 mole % of 2-phenylindanedione oxidation was delayed for 25 h. The oxidation of this hydrocarbon is inhibited by 2-*p*-nitro- and 2-*p*-methoxy-phenylindanediones. The causes of the antioxidant power of β-diketones were not elucidated. This problem has been examined in greater detail in a study[21,98] of the oxidation of tetrahydronaphthalene. An active hydrogen atom must be present at the 2-position for inhibiting activity to develop in diketones. Compounds that do not contain such an atom—e.g. 2-ethyl- and 2-methyl-2-phenylindanediones and the dimer of 2-phenylindanedione (II)—do not influence the oxidation. It was found also that the end of the induction period coincided with the instant at which the 2-phenylindanedione was almost completely exhausted. Separate experiments with pure tetralin hydroperoxide in chlorobenzene at 100°C showed that under these conditions decomposition of the hydroperoxide was not affected by 2-phenylindanedione. If a 0.0002 M solution of the latter in tetralin is added before the start of oxidation, an induction period of 100 min is observed.

If the same quantity of this diketone is added during oxidation, no induction period is observed, and the rate of oxidation is almost unchanged. Thus 2-arylindanediones inhibit the autoxidation of hydrocarbons as a consequence of reaction of the active hydrogen atom with peroxy-radicals.

Table 3. Induction periods in the oxidation of tetralin in the presence of substituted indane-1,3-diones.

Substituents	τ, min	Substituents	τ, min
2-Phenyl	100		
2-Naphth-1'-yl	18	4,5,6,7-Tetrachloro-2-phenyl	300
2-Naphth-2'-yl	300		
		2-(2,4,6-Trimethoxyphenyl)	0

A relation has been established between the reactivity of 2-arylindane-1,3-diones towards DPPH radicals and the antioxidant power of the diketones. Thus 2-(2,4,6-trimethoxyphenyl)indanedione (XVI), which does not react with DPPH and the *p*-methoxylated radicals, does not affect the rate of oxidation of tetraline; whereas 4,5,6,7-tetrachloro-2-phenylindanedione, which reacts with these radicals, produces a considerable induction period in the oxidation of tetralin. Table 3 lists the induction periods in the autoxidation of tetralin in the presence of various 2-arylindanediones (0.0002 M) at 100°C. Comparison of the induction period with the behaviour of the 2-arylindanediones towards DPPH shows at least a qualitative parallelism between the antioxidant power of the diketones and the mobility of the 2-hydrogen atom towards the free radical. The lower reactivity of 2-naphth-1'-ylindanedione (XIX) in comparison with 2-phenyl- and 2-naphth-2'-yl-indanedione (XX) is confirmed by its behaviour in the autoxidation of hydrocarbons.

Table 4. Reactivity of phenols.

Compound	k, M^{-1} min^{-1}	τ, min
Phenol	4.3 (19.6°)	75
1-Naphthol	8000 (15.5°)	2250
2-Naphthol	377 (19.0°)	330

It is interesting to draw an analogy between the above compounds and phenols and naphthols. Table 4 lists the rate constants for the reactions of these phenols with DPPH and the induction periods in the oxidation of gasoline in their presence[100]. It is evident that 1- and 2-naphthols are more reactive than phenol in radical reactions. A similar relation should apparently apply to the above 2-arylindanediones. The naphthyl ring system provides greater possibilities for delocalisation of the electron, and the corresponding 2-aryl-1,3-dioxoindanyl radicals should be more stable, so that hydrogen should be more easily detached from diketones containing a naphthyl ring system. However, this is observed only with 2-naphth-2'-ylindanedione: in the case of the naphth-1'-yl derivative the reactivity drops owing to a change in molecular configuration.

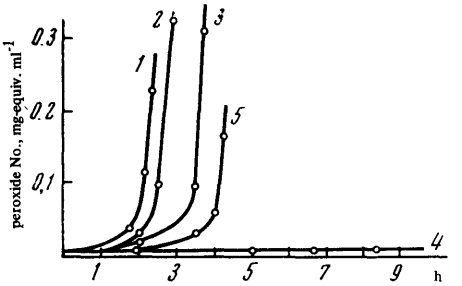


Figure 3. Kinetics of the oxidation of vegetable oil at 120°C in the presence of inhibitors: 1) no antioxidant; 2) 0.01 M ionol; 3) 0.01 M (I); 4) 0.01 M (XXI); 5) 0.001 M (XXI).

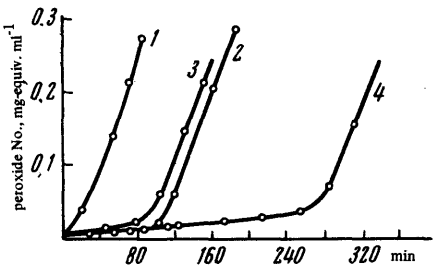
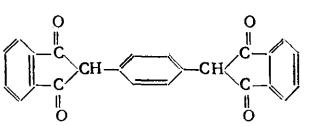


Figure 4. Kinetics of the oxidation of rendered fat at 120°C in the presence of inhibitors: 1) no antioxidant; 2) ionol (0.01 mole kg^{-1}); 3) (I) (0.01 mole kg^{-1}); 4) 2-*p*-hydroxyphenylindanedione (0.01 mole kg^{-1}).

Table 5. Inhibition of the oxidation of sunflower oil at 120°C.

Antioxidant	C, M	τ, min	ε	Antioxidant	C, M	τ, min	ε
None	—	126	—	(XXI)	10^{-2}	>600	19.2
Ionol	10^{-2}	152	1		10^{-3}	186	
(I)	10^{-2}	212	3.3				
				(VII: R = H)	10^{-2}	270	5.5

The antioxidant power of substituted 2-arylindanediones has been examined in detail[119] on the oxidation of sunflower oil and rendered fat. Fig. 3 illustrates the kinetics of oxidation of the oil at 120°C in the presence of equimolar quantities (0.01 M) of ionol, 2-phenylindanedione, and *p*-phenylene-2,2'-bisindane-1,3-dione



(XXI)

Fig. 3 shows that the substituted indanediones are more effective than the well known antioxidant ionol. Compound (XXI) exhibits an inhibiting effect at a concentration of 0.001 M, at which ionol is completely ineffective.

Hydroxylated 2-phenylindanediones, e.g. the *p*-hydroxy-derivative, were highly effective antioxidants for oils and fats. Fig. 4 illustrates the course of the oxidation of rendered fat at 120°C in the presence of ionol, 2-phenylindanedione, and 2-*p*-hydroxyphenylindanedione (each 0.01 mole kg^{-1}). Table 5 lists the induction periods and the efficiencies of certain diketones in the oxidation of sunflower oil. Antioxidant efficiency was calculated[120] by means of the formula

$$\varepsilon = \left(\frac{\tau - \tau_0}{C}\right)_{\text{init}} : \left(\frac{\tau_1 - \tau_0}{C}\right)_{\text{stand}}$$

where τ, τ_1, and τ_0 are the induction periods during oxidation of the substrate in the presence of the test compound and of the standard (ionol) and in the absence of an inhibitor respectively, and C is the inhibitor concentration.

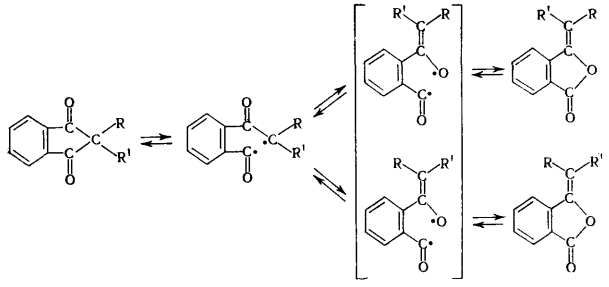
VII. 2-ARYLINDANE-1,3-DIONES AS STABILISERS FOR POLYMERS

The ability of 2-arylindanediones to inhibit the oxidation of hydrocarbons suggested that they could serve as stabilisers for polymers. The efficiency of several substituted 2-phenylindanediones as stabilisers was investigated in polyethylene and polypropylene[121]. Table 6 shows the dependence of the induction period in the oxidation of low-density polyethylene at 150°C on the structure and the concentration of the diketone (the induction period in the oxidation of unstabilised polyethylene is 105 min). The introduction of methoxy- and hydroxy-groups into 2-phenylindanedione enhances the antioxidant efficiency. Unfortunately, these workers[121] did not measure the change in molecular weight of the polymer during aging as a function of the antioxidant, which would have represented the efficiency of the stabiliser most fully and objectively.

Table 6. Dependence of induction period (min) in the oxidation of polyethylene on the structure and concentration of diketones.

Substituted indane-1,3-dione	Concentration, %		
	0.05	0.1	0.5
	induction period		
2-Phenyl	120	180	900
2-*p*-Methoxyphenyl	300	540	990
2-*p*-Hydroxyphenyl	540	840	2040
2-*p*-Chlorophenyl	110	120	780
2-(3,4-Dimethoxyphenyl)	330	570	1080
2-*p*-Dimethylaminophenyl	200	480	640
4-Hydroxy-5-methoxy-2-phenyl	390	660	1680
4,5-Dihydroxy-2-phenyl	490	840	1530
Ionol		610	

This work showed a slight photostabilising effect of substituted 2-phenylindanediones when polyethylene and polypropylene were exposed at 40°C to a PRK-2 lamp. The absorption maxima in the ultraviolet spectra of 2-arylindanediones are situated approximately in the same regions as in the spectra of known photostabilisers, and a most important practical problem is to select effective compounds and study the mechanism of their action[122]. Under the influence of light 2-phenylindanediones may undergo transitions involving keto–enol tautomerism. Light energy may be absorbed also by a different path. Substituted indane-1,3-diones are isomerised by ultraviolet radiation[123–125] into high yields of phthalide derivatives:



Substituted 2-phenylindanediones prevent the thermo-oxidative degradation and cross-linking of Capron [6-polyamide] film and bristle, largely preserving the physico-mechanical properties of these polymers at 200°C and the specific viscosity of the bristle at 150°C. Diketones containing hydroxy-groups in the benzene rings—2-*p*-hydroxyphenylindanedione and 4-hydroxy-5-methoxy-2-phenylindanedione—possess the strongest inhibiting power.

Although 2-phenylindanedione develops its antioxidant properties in saturated polymers (e.g. polyethylene), the effect is almost completely absent in unsaturated rubbers[68], owing to the relatively high reactivity of 2-aryl-1,3-dioxoindanyl radicals. A mixture of 2-phenylindanedione with 1,2,3,4-tetrahydro-2,2,4-trimethylquinoline was found to exert a certain synergic action in the oxidation of SKS-30 rubber[34]. This effect was assessed merely from the time variation in the relative amplitude of the nuclear magnetic resonance signal, without the application of unambiguous methods for proving synergy[129] and measuring the molecular characteristics of the polymer during aging.

Table 7. Induction periods in the oxidation of SKDL rubber in the presence of ionol and of 2-substituted indane-1,3-diones.

Substituent	τ, min.
Ionol	185
Phenyl	7
p-Hydroxyphenyl	24
4'-Hydroxy-3',5'-dimethylphenyl	230
4'-Hydroxy-3',5'-di-isopropylphenyl	34
4'-Hydroxy-3',5'-di-t-butylphenyl	125
3',5'-Diallyl-4'-hydroxyphenyl	50
4'-Hydroxy-3',5'-dimethoxyphenyl	240
3',5'-Dibromo-4'-hydroxyphenyl	20
4'-Oxocyclohexa-2',5'-dienyl	21
3',5'-Dimethyl-4'-oxocyclohexa-2',5'-dienyl	300
No antioxidant	3

p-Hydroxylated 2-arylindanediones (VII) containing a sterically hindered phenolic fragment are of the greatest interest[68] for stabilising unsaturated rubbers. Table 7 gives the induction periods τ in the oxidation of lithium butadiene rubber SKDL at 130°C in the presence of several diketones (VII) and methylenequinones (VIII) at a concentration of 0.02 mole kg^{-1} polymer.

The above results show that several indane-1,3-dione derivatives surpass the well known stabiliser ionol in efficiency of inhibition.

VIII. EFFECT OF 2-ARYLINDANE-1,3-DIONES ON RADICAL POLYMERISATION

In the presence of atmospheric oxygen 2-arylindane-1,3-diones, in contrast to phenols, accelerate the thermal polymerisation[130] of styrene at 100°C. The ability of substituted 2-phenylindanediones to influence the rate of polymerisation is directly related to their reactivity towards the stable radical 2-*p*-methoxyphenyl-2-phenyl-1-picrylhydrazyl: the highly reactive 4,5,6,7-tetrachloro-2-phenylindanedione (XVIII) has a considerable accelerating effect on polymerisation, but the relatively unreactive 2-(2,4,6-trimethoxyphenyl)indanedione (XVI) does not affect its kinetics. The introduction into the *para*-position of an electron-accepting substituent, e.g. a bromine atom, makes the 2-arylindanedione a stronger accelerator of polymerisation; on the other hand, 2-*p*-methoxyphenylindanedione, which contains an electron-donating substituent, has rather less effect than the unsaturated phenyl derivative on the rate of polymerisation. Like many phenols, 2-phenylindanedione does not change the rate of polymerisation in argon[131]. The polymerisation of styrene is actively initiated by the dimer (II), which breaks down into free radicals when heated in hydrocarbons[33]. The formation of polystyrene has been observed[64] also in the arylation of 2-phenylindanedione with diphenyliodonium chloride in the presence of styrene. Radicals of the triphenylmethyl type also accelerate the polymerisation of styrene[132].

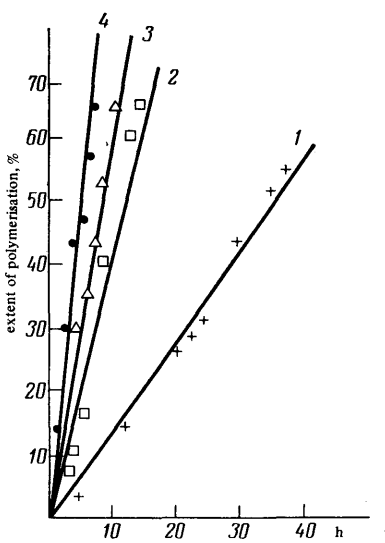


Figure 5. Dependence of rate of polymerisation of SKN-26 rubber on nature and quantity (part by weight) of activator: 1) no activator; 2) 0.2 trihydroxyethylamine; 3) 0.1 (I); 4) 0.2 (I).

The acceleration[133] of emulsion polymerisation in the production of butadiene–nitrile rubbers in the presence of 2-arylindanediones is of practical interest. The use of 0.2 part by weight of 2-phenylindanedione as activator triples the rate of polymerisation observed with the same quantity of trishydroxyethylamine. Fig. 5 illustrates the dependence of the rate of polymerisation on the nature and quantity of activator. In the production of SKN-26 butadiene–nitrile rubber 100% polymerisation is attained in 5 and 20 h respectively in the presence and in the absence of the above quantity of 2-phenylindanedione. The acceleration of emulsion polymerisation is due to the presence of 2-aryl-1,3-dioxoindanyl radicals formed by reaction with the polymerisation initiator—potassium persulphate:

$$2\Phi^- + S_2O_8^{2-} \rightarrow 2\Phi\cdot + 2SO_4^{2-}$$

The formation of dimers of type (II) from 2-arylindanediones has been observed[55] repeatedly in the presence of ammonium persulphate. The increase in the rate of polymerisation of styrene in the presence of 2-arylindanediones in air is also due to radicals resulting[21] from reaction of the β-diketones with oxidation products of styrene.

A second property of 2-arylindanediones of practical importance is their ability to act as chain-transfer agents. Various classes of organic compounds (hydrocarbons, alkenes, thiols, disulphides, amines, phenols, halogenated compounds, etc.) have been investigated[6] in chain-transfer reactions. A few active chain-transfer agents have been widely used in industry under the name regulators or modifiers. In the case of 2-arylindanediones chain transfer can be represented by the scheme

$$RM_n\cdot + \Phi H \xrightarrow{k_s} RM_nH + \Phi\cdot$$
$$\Phi\cdot + M \rightarrow \Phi M\cdot$$
$$RM_n\cdot + M \xrightarrow{k_p} RM_{n+1}\cdot$$

Measurements[134] of chain-transfer constants $C_S = k_S/k_p$ for a series of 2-arylindanediones in the thermal polymerisation of styrene at 100°C were made by Mayo's method[135] from the relation

$$\frac{1}{p} = \frac{1}{p_0} + C_s\frac{[\Phi H]}{[M]}$$

where p_0 and p are the degrees of polymerisation obtained in the absence of a regulator and with a molar ratio $[\Phi H]/[M]$ of regulator to monomer. The results in Table 8 show a fairly wide range of variation—from 0.0001 to 1.05—determined by the structure of the diketone.

Table 8. Chain-transfer constants of 2-substituted indane-1,3-diones.

Substituent	C_s	Substituent	C_s
	0.0044		
Phenyl	0.53	3',4'-Dimethoxyphenyl	0.64
Benzyl	0.058	*p*-Tolyl	0.57
o-Methoxyphenyl	0.01	*m*-Chlorophenyl	0.73
2',4'-Dimethoxyphenyl	0.01	*p*-Chlorophenyl	0.84
		p-Bromophenyl	0.87
2',4',6'-Trimethoxyphenyl	0.0017	3',4'-Dichlorophenyl	1.00
1'-Naphthyl	0.039	3',5'-Dibromophenyl	1.05
2'-Naphthyl	0.65		
p-Methoxyphenyl	0.80	2-Methyl-2-phenyl	0.0001
3',4'-Methylenedioxyphenyl	0.71	2-(3',5'-Dibromophenyl)2-methyl	0.014

Introduction of a phenyl ring into the indane-1,3-dione molecule increases the chain-transfer constant hundredfold, and produces a considerable change in its reactivity. Thus the half-wave potential of anodic oxidation is lowered[75], which is consistent with calculations of the energy of the highest occupied molecular orbital in the anionic form of β-diketones. Separation of the dioxoindanyl ring system

from the phenyl ring by a methylene bridge reduces the chain-transfer constant to one-tenth of its value. The position of the substituent in the phenyl ring has a considerable effect on the reactivity of substituted 2-phenylindanediones, the chain-transfer constants for the *ortho*-substituted 2-*o*-methoxyphenyl-, 2-(2,4-dimethoxyphenyl)-, and 2-(2,4,6-trimethoxyphenyl)-indanediones being far smaller than that for the unsubstituted phenyl derivative. The results[65,123,136] are consistent with the nuclear magnetic resonance spectra: introduction of a phenyl group into indane-1,3-dione increases the chemical shift of the active proton at position 2; introduction of an *ortho*-substituent into 2-phenylindanedione produces a decrease in the chemical shift.

As in the reaction with diphenylpicrylhydrazyl, 2-naphth-1'-ylindanedione (XIX) and 2-naphth-2'-ylindanedione (XX) exhibit different reactivities: (XIX) is less reactive than (XX) and the 2-phenyl compound.

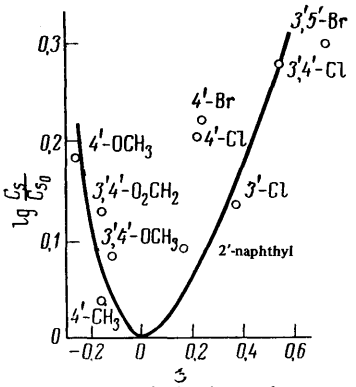
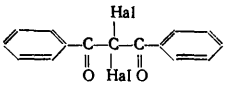


Figure 6. Correlation of chain-transfer constants for substituted 2-phenylindanediones in the thermal polymerisation of styrene, plotted in Hammett coordinates.

It is noteworthy that *meta*- and *para*-substituents in the 2-phenyl ring, independently of whether they are electron-donating or electron-accepting, increase the chain-transfer constant of the compounds in comparison with unsubstituted 2-phenylindanedione. Fig. 6 shows the Hammett plot of the relation obtained. These substituted derivatives have high chain-transfer constants, and surpass several known carriers in activity[6], but are inferior to thiols and certain disulphides[137].

2-Arylindane-1,3-diones containing halogen at position 2 are quite active in chain transfer in the thermal polymerisation of styrene. Compounds of this type have been tested also as modifiers of emulsion polymerisation in the production of polychloroprene[138] and butadiene rubbers[139]. 2-Bromo-2-phenylindanedione (0.6 part by weight) effectively controls the molecular weight of polychloroprene[138] during polymerisation at 50°C. Chain transfer occurs especially efficiently via the bromo-diketone in the initial stages of polymerisation, which is evidently not fortuitous. A disadvantage of 2-halogenated indane-1,3-diones as polymerisation regulators is that the halogen is positive in character[140] and easily detached in weakly alkaline medium, even in sodium hydrogen carbonate solution, for example. They will therefore lose their halogen by this side-reaction during emulsion polymerisation. On the basis of the above researches it has been suggested[141] that dibenzoyldihalogenomethanes



(XXII)

will be more effective regulators of radical polymerisation, free from the above disadvantages.

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The work on the radical reactions of 2-arylindane-1,3-diones examined above shows that β-diketones play an active part in reactions of practical interest. The capacity of substituted indane-1,3-diones for keto–enol tautomerism and the formation of intra- and inter-molecular hydrogen bonds makes this class of compounds attractive for the investigation of radical reactivity. There is every reason to suppose that further study of the radical reactions of 2-arylindanediones will give interesting theoretical and practical results.

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