1-Ethoxy-1,2,3,5,6-pentaphenylindene was secured by refluxing a 10% solution of the bromoindene in ethanol for one-half hour, and recrystallizing from benzene–petroleum ether; it melts at 175–176°.

Anal. Calcd. for $C_{41}H_{32}O$: C, 91.1; H, 5.9. Found: C, 91.2; H, 6.2.

Oxidation.—A mixture of 4 g. of the indene, m. p. 280°, 5 g. of chromium trioxide and 40 cc. of acetic acid was refluxed for one-half hour, and worked up by appropriate manipulation. It gave 2 g. of 4,5-diphenyl-*o*-dibenzoylbenzene V, and 0.4 g. of benzoic acid.

In a similar manner 2 g. of the hydrocarbon, m. p. 227°, was oxidized; it gave 1 g. of the diketone V and only sufficient benzoic acid for a melting point determination.

When 5 g. of the hydrocarbon, m. p. 222°, was treated by the same procedure, it gave 3 g. of the lactone X (R = C_6H_5), m. p. 184–185°.

Anal. Calcd. for $C_{39}H_{28}O_2$: C, 88.6; H, 5.3; mol. wt., 528. Found: C, 88.4; H, 6.1; mol. wt. (in benzene), 560.

The lactone is insoluble in sodium carbonate, but dissolves in alcoholic sodium hydroxide and is reprecipitated by mineral acid. It shows no activity in the Grignard machine; this failure to show addition is attributed to the *gem*-diphenyl group.

2,3,9,10-Tetraphenylanthracene XI (R = C_6H_5).—From the lactone: a suspension of 1 g. each of sodium amide and the above lactone in 10 cc. of *p*-cymene was refluxed for four hours, water added and the cymene distilled with steam. The solid product was filtered and crystallized from acetic acid, it melts at 324–325°, and shows a bluish-violet fluorescence.

Anal. Calcd. for $C_{38}H_{26}$: C, 94.6; H, 5.4; mol. wt., 482. Found: C, 94.4; H, 5.6; mol. wt. (in benzene) 486.

Employing the previously described procedure,[8] the same hydrocarbon resulted when the known 9,10-diol was reduced by potassium iodide in acetic acid.

The Triphenyl Indene Series.—Following the procedures in the literature,[9] 2,3,3-triphenylindanone, its enol-benzoate, oxido enol-benzoate, and ketol, m. p. 156° were prepared. In the case of the oxido enol-benzoate, a 1:1-addition product containing acetic acid, and melting at 125° crystallized from the reaction mixture.

Anal. Calcd. for $C_{36}H_{28}O_5$: C, 80.0; H, 5.2. Found: C, 79.9; H, 5.4.

On recrystallizing from benzene–petroleum ether, it at once gave the solvent-free product, m. p. 196°. Our analytical figures on the ketol were in exact agreement with those published. In the Grignard machine it showed one active hydrogen and one addition.

When either the oxido enol-benzoate, or the ketol was treated with sodium amide in cymene, by the procedure described above, the known 9,10-diphenylanthracene resulted. It was identical with an authentic specimen.[13]

Summary

The structures of three polyarylated indenes which were prepared by dehydration under acidic conditions of certain carbinols have been determined.

Two are rearranged to the third on being heated to 420°.

One of the hydrocarbons is converted into a lactone by the action of chromium trioxide; the lactone gives a derivative of 9,10-diphenylanthracene on heating with sodium amide. The nature of these and of other rearrangements encountered is discussed.

---

[13] Simonis and Remmert, *Ber.*, **48**, 208 (1915).

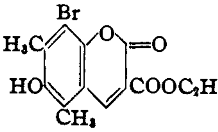
ROCHESTER, NEW YORK RECEIVED JUNE 30, 1943

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction between Quinones and Metallic Enolates. XVIII. Mechanisms[1]

BY LEE IRVIN SMITH, R. T. ARNOLD AND JOSEPH NICHOLS

Four halogenated alkylquinones have now been studied with which there is opportunity for the two reactions with sodiomalonic ester, replacement and formation of a coumarin derivative, to occur simultaneously. From bromotrimethylquinone, only a coumarin was obtained, and of the three possible coumarins, only one, I, resulted.[2] Of the three dibromodimethylparabenzoquinones, the meta compound[3] gave only a coumarin, whereas the ortho-[4] and para-isomers[1] reacted only by replacement. In these last two compounds one or both halogen atoms could be replaced by malonic ester residues; the first quite readily, but the second only with difficulty and in poor yield. Smith and Austin[4] concluded that the important factor in determining the course of the reaction of the dibromoquinones was the relative position of the bromine atoms; they did not develop this thesis, which was, in fact, an outgrowth of the speculations of Smith and Johnson[2] as to why only one coumarin was formed from bromotrimethylquinone.



I

It is obvious that the controlling factor is the lability of the bromine atoms concerned; when these are highly active, replacement becomes rapid, and when the bromine atoms are unreactive, time becomes available for a pentad-enolization of the quinone[5] with resultant addition of malonic ester to form a coumarin. By application of the concept of resonance to these quinones, it is possible to explain and to correlate all the facts so far known with regard to the course of these reactions. Some of the contributing resonance forms of dibromo-*p*-xyloquinone II may be represented as follows

---

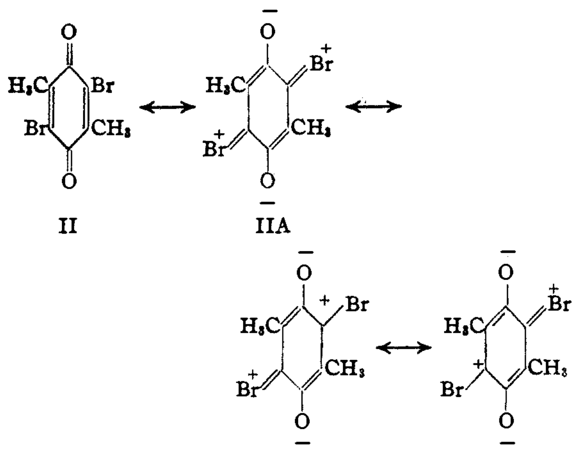
[1] XVII, Smith and Nichols, THIS JOURNAL, **65**, 1739 (1943).

[2] Smith and Johnson, *ibid.*, **59**, 673 (1937).

[3] Smith and Byers, *ibid.*, **63**, 612 (1941).

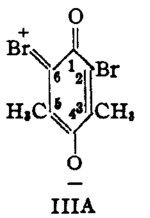
[4] Smith and Austin, *ibid.*, **64**, 528 (1942).

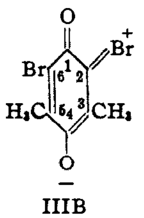
[5] (a) Fuson, *Chem. Rev.*, **16**, 1 (1935); (b) Smith and Horner, THIS JOURNAL, **60**, 676 (1938).

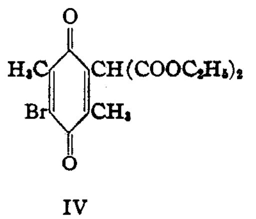

II IIA IIB IIC

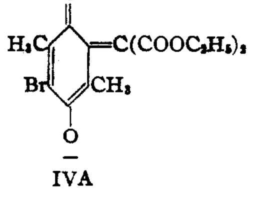
Structures IIB and IIC are similar; therefore they exist in complete resonance and possess enhanced stability. It is well known that resonance effects in substitution reactions are especially pronounced when two groups, one an electron acceptor and the other an electron donor, are present in the same molecule, as in II, in which the oxygen atoms are capable of absorbing the electrons contributed by the halogen atoms. In the above structures for II, the resonance effect serves to place a positive charge on the carbon atom holding the bromine atom. This makes possible an attack by the malonic ester anion upon this carbon atom, with release of a bromide ion, *i. e.*, the replacement of a weak base (bromide ion) by a stronger one (malonic ester ion). All of these considerations, applied to dibromo-*o*-xyloquinone, lead to the same conclusion—replacement of the halogen atoms should be relatively easy.

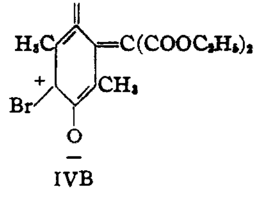
However, no quinoid resonance structures of the type shown for II are possible in the case of dibromo-*m*-xyloquinone III, for these would be metaquinoid in nature; the most important resonance structures of the meta dibromoquinone are IIIA and IIIB. In order for a positive charge on carbon atom number 2 (6) to be effective, both halogen atoms must exist in quinoidal relationship to each other. In the quinone III, the total positive charge resulting from resonance involving the double bonds (C_{2-3} and C_{5-6}) and the carbonyl group (C_4) is shared equally between C_2 and C_6. As a result the charge associated with either of these carbon atoms is too small to facilitate the replacement of the bromine atom by the malonic ester anion (anionoid reagents). However, when two bromine atoms in a quinone are attached to carbon atoms ortho or para to each other, the residual positive charge associated with the carbon atoms becomes much greater because both carbonyl groups are involved in the resonance The replacement reaction then becomes dominant, and little or no coumarin is formed. It is the absence of resonance forms of the *m*-dibromoquinone with "active" bromine atoms which inhibits the replacement reaction and thus makes possible the formation of a coumarin.


IIIA


IIIB

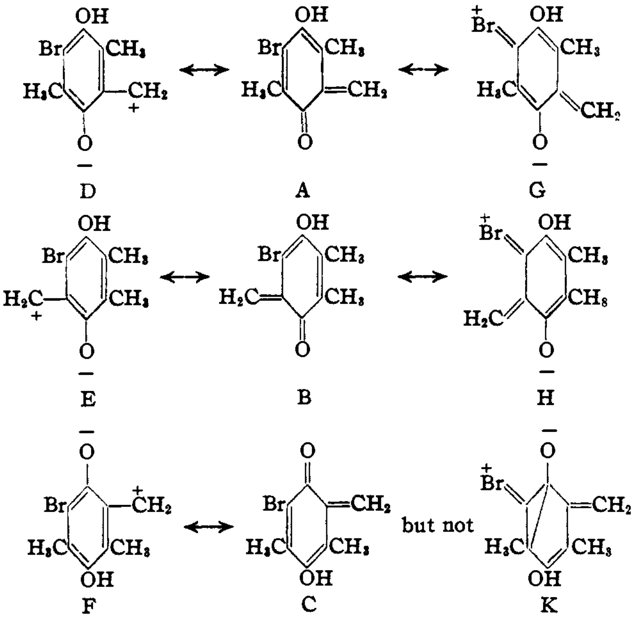

IV


IVA


IVB

Replacement of the second bromine atom in dibromo-*p*-xyloquinone by a malonic ester residue, on the basis of these considerations, should be difficult. The quinone-malonic ester IV exists in solution as a negative ion; this quinone is actually a stronger acid than is malonic ester. Hence a situation arises in which the replacement of the second bromine atom by a malonic ester ion requires the interaction of two substances which have like charges. As a result, there is a strong coulombic force which repels the malonic ester ion, and, for a reaction to occur, the molecules must be sufficiently activated to overcome this electrical barrier. Even though replacement of the second bromine atom is slow, formation of a coumarin is not to be expected, for enolization of IV would certainly involve the malonic ester hydrogen rather than the hydrogen of one of the methyl groups, and the intermediate enol would be IVA. In IVA the conjugated system is too highly hindered for a 1,4-addition to occur. Moreover, one of the important resonance forms of the anion of IV is IVB, in which the bromine atom can undergo replacement, but which cannot enter into the reaction leading to a coumarin. Replacement of the second bromine atom, therefore, is the only reaction that can occur when IV reacts with sodiomalonic ester.

Of the three possible pentad-enolic forms of bromotrimethylquinone, two can exist in two resonance forms each, but the third can exist in but one resonance form. In order to form a coumarin, malonic ester must add 1,4 to a conjugated system which includes the carbonyl and methylene groups present in A, B, or C, and this reaction must proceed via the resonance forms D, E, or F in which the positively charged methylene group attracts and binds the malonic ester residue. In the enolic forms A and B, the presence of the respective resonance forms G and H diminishes the importance of the resonance forms D and E. Of greater importance, however, is the fact that in A and B the positive charge is shared



by the bromine atom and the methylene group, thus dispersing the charge and decreasing the effective charge upon the methylene group. But in C, the absence of form K allows the positive charge to be concentrated upon the methylene group; hence, when a coumarin is formed, it is derived from C and not from A or B. And that the reaction of this quinone with sodiomalonic ester will result in formation of a coumarin and not in replacement of the bromine atom follows from the fact that there is present in this quinone no second group, such as another halogen atom, which can contribute to the resonance effect and so place, upon the carbon atom holding the halogen, a large enough positive charge for a replacement to occur. Even though the enolic forms A and B exist in a greater number of resonance forms than does enolic form C, with a consequence that A and B may be present in solution in greater concentration than C, this merely decreases the rate, but does not change the course, of the reaction between the quinone and sodiomalonic ester.

These generalizations have even broader implications than those just defined, for it is possible to extend these ideas not only to cover the reactions between enolates and all quinones, but also to cover the attack of anionoid reagents upon all hetero conjugated systems, open-chained or cyclic, including those in which the double bond is in an aromatic ring. All of the reactions may be regarded initially, and in the classical sense, as 1,4-additions to a conjugated system of the quinone, but which particular conjugated system will be involved will depend upon the nature of the groups attached to the quinone and also upon the nature of the attacking anionoid reagent. The initial step involves a polarization of the conjugated system, so that the β-carbon atom acquires a "positive charge." This positive carbon atom then attracts the anionoid reagent from the solution. If, now, the group originally attached to this carbon atom is one which cannot be readily eliminated as a negative ion (alkyl group), there follows either a reversal of the addition (*e. g.*, of the malonic ester ion), in which case no reaction occurs at all (the alkyl group is ethyl), or a new conjugated system is formed by pentadenolization (the alkyl group is methyl) and a coumarin results. But if the group originally attached to the β-carbon atom can be eliminated readily as an ion (bromine), this exchange reaction completes itself and replacement by the malonic ester residue occurs. When the group originally attached to the β-carbon atom cannot be eliminated as a stable negative ion (hydrogen), but can undergo some other change such as enolization, which will stabilize the molecule, then ordinary 1,4-addition of malonic ester occurs, but in this case the product is a *hydroquinone*,[1,6,7] and not a quinone as it is when the group (bromine) can be eliminated as a stable negative ion. It is interesting and significant that even alkyl groups may enter into these replacement reactions if the attacking reagent is of the proper type. Thus a *neutral* reagent which contains an atom holding, in addition to a lone pair of electrons, at least one hydrogen atom (primary or secondary amines, but not tertiary amines), may coördinate at the positively charged β-carbon atom and then expel the alkyl group, together with the hydrogen atom of the reagent, as a *neutral molecule*, a hydrocarbon. Thus Hoffmann[8] and later Boters[9] found that when dibromothymoquinone reacted with neutral molecules such as aniline, *p*-toluidine, and anisidine, the methyl group of the quinone was replaced by a substituted amino group; when this same dibromothymoquinone reacted with the ionic sodiomalonic ester, however, a bromine atom (ortho to the methyl group) was replaced. Anslow and Raistrick[10] have observed a similar replacement of a methyl group by a methylamino group in the reaction between an alcoholic solution of methylamine and 2-methyl-5-methoxy-1,4-benzoquinone or 2-methyl-3,5-dimethoxy-1,4-benzoquinone. In the case of the first quinone, the methoxyl group was simultaneously replaced; but in the second quinone only one (ortho to the methyl group) methoxyl group reacted.

Most of the common substitution reactions of aromatic compounds involve an attack of a cationoid reagent upon the nucleus, and the ordinary rules for orientation of the substituents have been

---

(6) Smith and MacMullen, THIS JOURNAL, **58**, 629 (1936).

(7) (a) Smith and Kaiser, *ibid.*, **62**, 133 (1940); (b) Smith and King, *ibid.*, **65**, 441 (1943).

(8) Hoffmann, *Ber.*, **34**, 1558 (1901).

(9) Boters, *ibid.*, **35**, 1502 (1902).

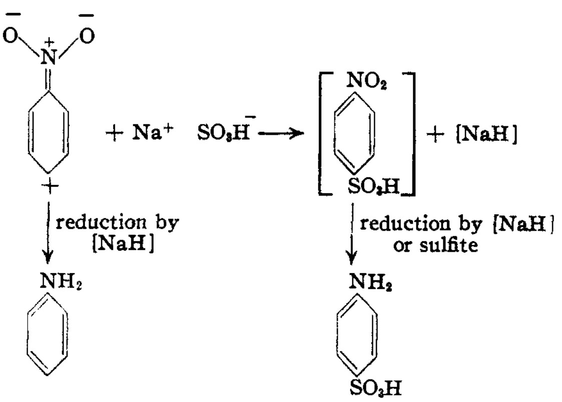
(10) Anslow and Raistrick, *J. Chem. Soc.*, 1446 (1939).

formulated as a result of a study of these reactions. But when the attacking reagent is anionoid in nature, these orientation effects are reversed, and aromatic compounds having carbonyl or nitro groups attached to the ring system react at the ortho and para positions. The reactions follow courses exactly paralleling those outlined for the reactions between quinones and enolates; the first step consists of an attack by the reagent at the β (ortho) or δ (para) carbon atom of a strongly polar resonance form. The second step consists of the expulsion of a negative ion or a neutral molecule, which is replaced by the entering group. In a quinone, this allows the quinoid ring system to be retained except when the group replaced is hydrogen; in this case, the system can stabilize itself by a tautomeric shift to the stable benzenoid structure, a hydroquinone results, and a negative hydride ion is not eliminated. But in an aromatic compound, replacement of hydrogen by an anionoid reagent necessitates elimination of hydrogen essentially as a hydride ion if the stable benzenoid form is to be retained. The expulsion of the hydride ion results in reduction of some component of the reaction mixture and often gives rise to "disproportionations" in reactions of this sort; it is well known that an oxidizing agent must be included as one of the reactants in order to obtain good results in anionic substitutions.

Thus nitrobenzene reacts with sodium hydroxide,[11] potassium carbazole[12] and sodium piperidinide[13] to give substitution products, and in each case the anionoid reagent attacks the para carbon atom with the expulsion of the thermodynamically unstable negative hydride ion. In a similar fashion, fusion of sodium anthraquinone-β-sulfonate with alkali produces alizarin, and a second hydroxyl group is introduced. As already mentioned, the presence of an oxidizing agent (air, potassium chlorate, etc.) prevents, to some extent, side reactions resulting from the attack of the strong reducing agent which is eliminated. Similar reactions occur when hydroxylamine acts as an anionoid reagent, but in this case obviously no oxidizing agent is required.[14]

It is well known that, in hindered conjugated systems of the proper sort, a double bond of an aromatic nucleus may participate in addition of Grignard reagents, but here again the first product is a very sensitive substance and it is only after this product has regained its aromatic structure by oxidation that it becomes stable.[15]

The Piria reaction follows a similar course; it has been demonstrated that sulfamic acids are not intermediates in this reaction,[16] and the reaction most likely involves an initial attack upon the nitro compound by the anionoid reagent.



Because of the presence of a second carbonyl group, and the ability of certain of the addition products to rearrange to stable aromatic systems (hydroquinones), quinones may react with anionoid reagents in every possible way. These reactions are, however, but special cases of the reactions of conjugated systems in general. A methylquinone such as duroquinone is capable of two types of resonance. There is first a resonance within the quinone molecule itself, which determines the course of the "pentad-enolization." After such an enolization occurs, it is followed by a resonance within the pentad-enolic form itself. The first type of resonance appears in many analogs of the quinones, in open-chained compounds and in the aromatic series, and its effects constitute the basis for the concept of vinylogy, which, although very useful, is limited. It seems better to adopt the more inclusive point of view that vinylogy is but a manifestation of resonance.

When the reactions of conjugated systems in general, and of quinones in particular, with anionoid reagents are regarded from the point of view expressed in this paper, and in the light of modern electronic concepts,[17] it becomes possible not only to recognize the possible reactions, but also to evaluate to some extent the factors which influence each of them.

Summary

The behavior of various bromopolymethylquinones toward sodiomalonic ester and other anionoid reagents has been explained and correlated by means of a theory based upon resonance effects, and it has been pointed out that this theory is capable of correlating the behavior of hetero conjugated systems in general toward anionoid reagents.

MINNEAPOLIS, MINNESOTA RECEIVED MAY 6, 1943

---

(11) Wohl, *Ber.*, **34**, 2444 (1901).

(12) Montmollin, *Helv. Chim. Acta* **6**, 94 (1923).

(13) Bradley and Robinson, *J. Chem. Soc.*, 1254 (1932).

(14) Meisenheimer and Patzig, *Ber.*, **39**, 2533 (1906).

(15) See Fuson, Armstrong and Speck, *J. Org. Chem.*, **7**, 297 (1942), for one of the several examples in the literature.

(16) Hunter and Sprung, THIS JOURNAL, **53**, 1443 (1931).

(17) Robinson, "An Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," published by the Institute of Chemistry of Great Britain and Ireland, 1932.