This review is devoted to research on the synthesis, reactivities, practical application, and structural problems of compounds of the phthalone series, primarily pyrophthalones and quinophthalones. The properties and peculiarities of the structures of the indicated compounds are compared with structural analogs that contain other heterocyclic substituents and other \( \beta \)-dicarbonyl systems and also with other betainelike derivatives of \( \beta \)-dicarbonyl compounds. Problems in the development of the chemistry of phthalones are discussed.

Indane-1,3-dione derivatives that contain a heterocyclic nitrogen-containing substituent, the nitrogen atom of which is in the \( \alpha \) position with respect to the indanenedione residue and consequently, in direct conjugation with the tautomeric \( \beta \)-dicarbonyl system, connected to the methylene group, are called phthalones. Substituents of the necessary type include 2-pyridyl (pyrophthalones), 2-quinolyl (quinophthalones), 2-benzimidazolyl, 2-benzothiazolyl, etc.

Several limiting structures — intraionic (betainelike) (A), aminovinylcarbonyl (with disruption of the cyclic delocalization of the \( \pi \) electrons i.e., the "aromaticity" of the heteroring) (B), and enol (C) — can be written for phthalones. An intramolecular hydrogen bond is formed in each of the three cases. Frequently, without going into the fine points of structures A, B, and C, phthalones with a stabilized "pseudoaromatic" enol chelate ring (D) are depicted. The problem of the greater or lesser contribution of the above-enumerated limiting structures to the real structure of the phthalones must be studied and discussed concretely in each case as a function of substituents \( R \).

In most cases the data necessary for this are not yet available. For this reason, in those cases where the equation of the fine structure is not discussed, it seems simpler to use the conventional depiction of the dicarbonyl system (E).

In a broader sense, betainelike derivatives of any \( \beta \)-dicarbonyl compounds (with an onium heterocyclic substituent connected to the active methylene group) in which there is direct conjugation between the anionic portion of the \( \beta \)-dicarbonyl residue and the onium heteroatom acting counter to the total charge localization can be called compounds of the phthalone type. Heteroatoms can also be found in rings condensed with the aryl residue.
Phthalones are interesting in that they absorb light intensively in the visible region (yellow and orange dyes). In addition to a study of the interrelationship between the structure and the color character, an essential problem in the chemistry of phthalones is their fine structure and the reactivities and electrophysical properties that depend on this problem. The possibility of obtaining not only dyes and organic semiconductors but also new biologically active substances on the basis of phthalones seems attractive.

Syntheses of Phthalones

The principal method for the synthesis of phthalones is acylation of the reactive \(\alpha\)-or \(\gamma\)-methyl groups of heterocyclic bases by derivatives of phthalic acid or its structural analogs. The "phthalone reaction" — direct condensation of heterocyclic bases with phthalic anhydride, which was first described in 1882 [1, 6] — is the simplest and most general method. Other synthetic methods are applicable only in unique cases.

The quinophthalone formula proved in the first studies [5, 6] did not make it possible to make a choice between the isomeric quinaldylidenephthalide and quinolylindane-1,3-dione structures. The observation that, as in the bromination of arylidenephthalides, hydrogen bromide is not evolved in the reaction of bromine with quinophthalone led to the conclusion that phthalones have arylidenephthalide structures [7]. This sort of structure was in better agreement with the concepts of the reactivity of phthalic anhydride and the reasons for the chromaticity of the substances [8]. In a number of systematic investigations [8-21] phthalone condensation and the reactions of phthalones were studied, and isomeric side products were isolated in condensations with quinaldines ("isoquinophthalones"). A product (IIIa), which is probably in equilibrium with open form IIIb \([\alpha\)-(2-quinolyl)acetophenone-o-carboxylic acid], is formed at up to 130°C. When the addition product is heated to 160°C water is split out to give quinaldylidenephthalide (isoquinophthalone) (II). The latter is soluble in alkali, and acidification of solutions of it gives acid IIIb, which does not form II reversibly on heating but is converted to 2-(2-quinolyl)indane-1,3-dionequinophthalone (I). Isoquinophthalone II decomposes above its melting point (187°C) to give only very small amounts of quinophthalone I. Consequently, II is a side product rather than an intermediate in the phthalone condensation, and, like other arylidenephthalides, is converted to an indane-1,3-dione (quinophthalone) derivative only on reaction with alkoxide. Thus an indane-1,3-dione derivative structure was proved definitively for phthalones. Earlier studies of phthalones have been reviewed [22]. However, inaccuracies are encountered considerably later in the literature (for example, see [23, 24]). (See scheme on following page.)

The conditions of the phthalone condensation — heating phthalic anhydrides with quinaldines, picolines, and other heterocyclic bases containing active methylene groups at 180-250°C in the presence of zinc chloride — were not improved to any great extent in the subsequent studies. It was ascertained that the use of a catalyst (ZnCl₂) does not affect the yields of quinophthalones [25]. It has been proposed that the condensation be carried out in high-boiling solvents (o-dichlorobenzene [26], trichlorobenzene [27], nitrobenzene [28, 29], 1-chloronaphthalene [28], diphenyl, diphenylmethane, and diphenyl ether [30]). Condensation to give quinophthalones also occurs in dimethylformamide (DMFA) [31]. Quinophthalones are not formed in inert solvents at the boiling point of DMFA (153°C).

The phthalone condensation is an extremely general reaction and has been carried out successfully with substituted phthalic anhydrides containing halogenes, a nitro group, and a carboxyl group, with pyromellitic dianhydride, with 3,6-dithia-3,4,5,6-tetrahydrophthalic