The mechanism of synthesis of acridones based on treatment of diphenylamine-2-carboxylic acid with phosphorus oxychloride is considered. It is established that triphenylamine-2-carboxylic acid and the aniline of diphenylamine-2-carboxylic acid, when treated with phosphorus oxychloride, give high yield of 10-phenylacridone and 9-anilinoacridone respectively. The hitherto undescribed N-(o-chlorobenzoyl)diphenylamine-2-carboxylanilide is obtained by reacting phenylanthranilamide with o-chlorobenzoyl chloride, or by heating o-chlorobenzanilide with copper powder in nitrobenzene.

It is known that halogen compounds of phosphorus, particularly phosphorus oxychloride, find extensive application in the preparation of acridones and chloroacridones from diphenylamine-2-carboxylic acids. However, the literature records contradictory views about the mechanism of this reaction. Some authors [2-6] consider the acridone synthesis to involve intramolecular alkylation, via formation of halogenoanhydrides. Other authors [7, 8] consider that acridine ring closure with diphenylamine-2-carboxylic acid (I) proceeds via formation of N-phenylanthranilic acid lactam (II), or via a stage of formation of diphenylamine-2-carboxylic anhydride (III) or its rearrangement product N-phenylanthranil-N'-phenylanthranilic acid (IV). With the latter, 9, 10-acridylacridone (VI) may be a side product. Compounds II-IV were not isolated as intermediates. Up to the present views which have been put forward [7, 8] have not been extensively tested experimentally.
Starting from the idea that the \( \beta \)-lactam II is an intermediate in the formation of an acridone, an attempt has been made to develop an acridone synthesis based on o-chlorobenzoic acid anhydride (VII). It was assumed that under the conditions of the Ullmann reaction anilide VII gives the \( \beta \)-lactam II, which is then converted into the acridone V. However, experiments did not support this view, and the reaction, instead of being intramolecular, is intermolecular, and leads to formation of N-(o-chlorobenzoyl)diphenylamine-2-carboxylic anilide (VIII). When the latter was treated with concentrated sulfuric acid, aniline, o-chlorobenzonic acid, and acridone V could be isolated from the reaction products and identified. The structure of anilide VII was also demonstrated by a synthesis from the opposite direction, diphenylamine-2-carboxylic anilide (IX) being heated with o-chlorobenzoic chloride (X).

Substituted diphenylamine-2-carboxylic acids, viz., triphenylamine-2-carboxylic acid (XI) and diphenylamine-2-carboxylic anilide (IX), were also brought into the sphere of investigation. According to the views put forward, these compounds should not undergo acridone ring closure.

Thus, acid XI lacks hydrogen at the nitrogen atom, which naturally excludes formation of the \( \beta \)-lactam II, as well as formation of type IV compounds. The anilide group of anilide IX precludes the possibility of formation of the anhydride III. Good results are obtained when phosphorus oxychloride acts on acid XI and anilide IX, these being converted, respectively, to 10-phenylacridone (XIII) and 9-anilinoacridine (XV). Evidently, these conversions can be ascribed to intramolecular acylation, the reactions being

\[
\begin{align*}
\text{XI} & \rightarrow \text{XII} & \text{XIII} \\
\text{IX} & \rightarrow \text{XIV} & \text{XV}
\end{align*}
\]

In these transformations, the halogenoanhydride XII and the imidochloride XIV are the intermediates. Regarding possible formation of the latter see [9]. Experiments which have been carried out make it possible to conclude that the mechanism [2, 3] put forward applies both to free diphenylamine-2-carboxylic acid and its nitrogen- and carboxyl-substituted derivatives. The present results do not support the hypothesis of intermediate formation of the \( \beta \)-lactam II in acridone ring closure. It is considered that no general significance is to be attached to conversion of diphenylamine-2-carboxylic anhydride III and its rearrangement product IV to the acridone V.

**EXPERIMENTAL**

\textbf{N-(o-Chlorobenzoyl)diphenylamine-2-carboxylic anilide (VIII).}

a) 12 g VII, 8.3 g roasted potash, 0.4 g copper powder, and 40 ml nitrobenzene are refluxed for two hours, the nitrobenzene steam-distilled off, and the precipitate filtered off, and air-dried. Yield 11 g (89.5%). It is soluble with difficulty in alcohol, benzene, and acetone. Prisms (from glacial acetic acid), mp 214-215°.

b) 2.3 g IX and 1.5 g X are dissolved in 15 ml benzene, and refluxed for four hours. The benzene is distilled off, the residue treated with 10% soda solution, and crystallized from glacial acetic acid. Yield 2.5 g (73.5%) mixed mp with the compound from the previous experiment undepressed. Found: N 6.68, 6.31%. M 402, 415.7. Calculated for \( \text{C}_{26}\text{H}_{19}\text{ClN}_{2}\text{O}_{2} \): N 6.57%. M 426.8.

Conversion of VIII with conc. \( \text{H}_{2}\text{SO}_{4} \). 2 g VIII in 6 ml conc. \( \text{H}_{2}\text{SO}_{4} \) are heated for four hours on a water bath. The reaction products are poured into 20 ml boiling water, boiled for a few minutes, and cooled, and the precipitate is filtered off. Soda is added to the hot solution, which is crystallized from nitrobenzene. Yield 0.6 g V, mp 354° [10]. The acid filtrate gives the carbamylamine test for aniline. Acidification of the soda extract gives o-chlorobenzoic acid, mp and mixed mp with an authentic specimen 140°.