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# ELECTROÖRGANIC PREPARATIONS XIX. PREPARATION OF ARYL-Ψ-PHTHLAZINONES

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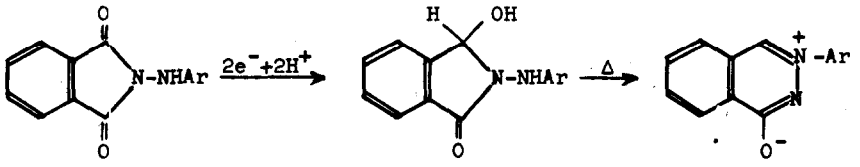
3-Aryl-Ψ-phthalazinones (1) (anhydrides of 3-aryl-1-hydroxy-phthalazinium hydroxides) have been prepared from the 2-aryl-4-hydroxy-1,2-dihydrophthalazine-1-acetic acids (2,3) obtained through some steps from 2-naphthol-1-sulfonic acid. The final elimination of acetic acid proceeds best when the aryl group contains electron attracting groups. This letter describes another route for the preparation of aryl-Ψ-phthalazinones.

Like other phthalimides N-arylaminophthalimides (I) can be reduced electrolytically at a mercury cathode to hydroxyphthalimidines (II) (4); often this reduction also can be effected with sodium borohydride. On heating, the N-arylamino-3-hydroxyphthalimidines lose water and rearrange to 3-aryl-Ψ-phthalazinones. This transformation can be effected e. g. by heating the hydroxyphthalimidine to about 120° or by boiling an aqueous solution of the compound for some hours. In Table 1 are given the melting points of some compounds prepared by this method.




I II III

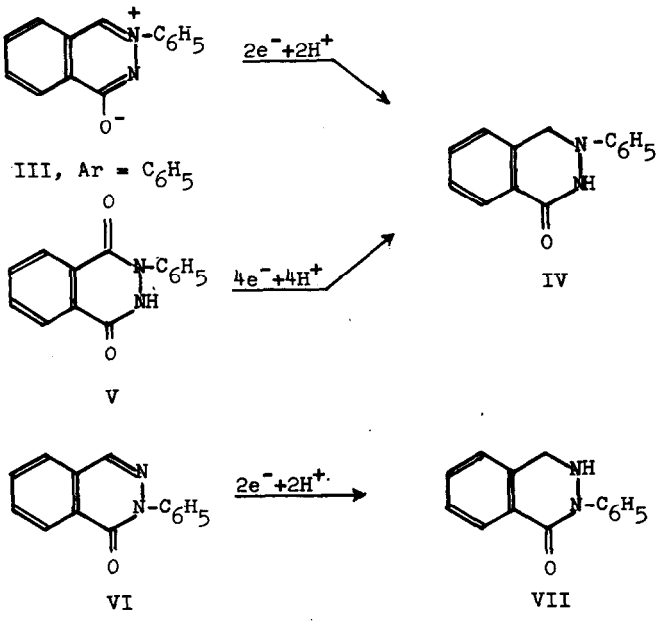
Table 1

Melting Points of Some N-Arylaminophthalimides (I), N-Arylaminohydroxyphthalimidines (II), and 3-Aryl-4-phthalazinones (III). *)

| Ar | I | II | III |
|---|---|---|---|
| $C_6H_5$ | 184° | 148° | 210° |
| o-$CH_3C_6H_4$ | 202° | 151° | 201° |
| m-$CH_3C_6H_4$ | 170° | 154° | 184° |
| p-$CH_3C_6H_4$ | 197° | 131° | 215° |
| 2-naphthyl | 184° | 162° | 245° |

*) Satisfactory analyses have been obtained for all the new compounds in Table 1.

The formulation of the product (III) of the rearrangement as the anhydride of 1-hydroxy-3-aryl-phthalazinium hydroxide is substantiated by the empirical formula, the absence of a carbonyl frequency in the IR-spectrum, the polarographic behaviour, which resembles that of other phthalazinium compounds and not that of e. g. diaziridines, and by the reductions described below.




III, Ar = $C_6H_5$

IV

V

VI

VII

3-Phenyl-4-phthalazinone-1 (III, Ar = $C_6H_5$) can in acid solution be reduced in a two-electron reduction at controlled potential to 3,4-dihydro-3-phenyl-1(2H)-phthalazinone (IV), m. p. 221°. The same compound can be obtained by a four-electron reduction of 2,3-dihydro-2-phenyl-1,4-phthalazinedione (V). A phenyldihydrophthalazinone (VII), m. p. 157°, different from the above mentioned is obtained in a two-electron reduction in acid solution of 2-phenyl-1-phthalazinone (VI).

N-Aminophthalimide and N-hydroxyphthalimide ("phthaloxime") can also be reduced electrolytically to the corresponding hydroxyphthalimidines. On heating, these compounds rearrange, the former to 1(2H)-phthalazinone and the latter to phthalimide.

Details on the reductions and rearrangements will later be published elsewhere.

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