INVESTIGATIONS IN THE FIELD OF PERINONE COMPOUNDS

I. Preparation of Perinones from Peri-Dinitro Compounds

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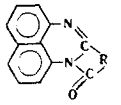
A simple method for preparing perinones from peri-dinitro compounds has been obtained. It has been shown that the reaction takes place via the formation of naphthalene-1, 8-diamine and 2-(2'-carboxyphenyl)-perimidine.

The reaction of aromatic peri-diamines with dicarboxylic acid leads to the formation of perinones with the general formula I, where R represents a bivalent aliphatic or aromatic radical. The perinones are used mainly for the bulk dyeing of synthetic fibers.



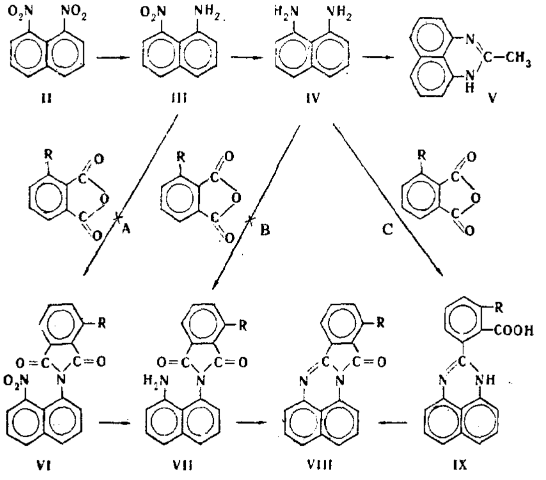
I

We have found a convenient method [2] for obtaining these compounds which consists in the simultaneous treatment of a peri-dinitro compound with iron powder and an aromatic ortho- or peri-dicarboxylic acid anhydride at an elevated temperature in acetic acid.

We set ourselves the aim of elucidating the sequence of chemical transformations of the peri-dinitro compound into the perinone that take place under the conditions of the method found.

The mechanism of the formation of the perinones from peri-dinitro compounds or peri-diamines and aromatic dicarboxylic acids has not been discussed in the literature previously. There is some analogy in the case of the synthesis of an aroylenebenzimidazole from o-phenylenediamine and naphthalic anhydride, but Krasovitskii's conclusions concerning the intermediate formation of 2-(8'-carboxy-1'-naphthyl)benzimidazole [3] contradict the results of Arient and Morgan [4] according to which this reaction takes place via N-(2'-aminophenyl)naphthalimide.

The formation of a typical perinone from 1, 8-dinitronaphthalene and phthalic anhydride in acetic acid in the presence of a reducing agent may be represented by the scheme



R = –H; –Cl

Using known methods, we have synthesized 1-amino-8-nitronaphthalene (III), naphthalene-1, 8-diamine (IV) [6], 2-methylperimidine (V) [7], 1-nitro-8-phthalimidonaphthalene (VI) [8], and 2-(2'-carboxyphenyl)perimidine (IX) [1]. Our attempts to obtain the previously unknown 1-amino-8-phthalimidonaphthalene (VII) by reducing compound VI with various reducing agents (iron in acetic acid, stannous chloride in aqueous alcohol, hydrogen, and hydrazine in aqueous organic solvents in the presence of palladium on carbon) led to the final reaction product—the phthaloperinone VIII.

In the synthesis of the phthaloperinone VIII from 1, 8-dinitronaphthalene and phthalic anhydride in acetic acid in the presence of iron powder under mild conditions, we took samples of the reaction mixture periodically and chromatographed them on paper in comparison with compounds II–VI, VIII, and IX. The table gives the R_f values of compounds II–VI, VIII, and IX, and also the time of their appearance in and disappearance from the reaction mixture.

Results of Chromatography

Compound	Name	R_f	Time, hr	
			of appearance	of disappearance
II	1,8-Dinitronaphthalene	0.41	—	10
III	1-Amino-8-nitronaphthalene	0.69	0.5	14
IV	Naphthalene-1,8-diamine	0.92	0.5	14
V	2-Methylperimidine	0.98	1	Did not disappear
VI	1-Nitro-8-phthalimidonaphthalene	0.28	Did not appear	Did not appear
VIII	Phthaloperinone	0.06	1.5	Did not disappear
	11-Chlorophthaloperinone	0.31	1	Did not disappear
IX	2-(2'-Carboxyphenyl)perimidine	0.95	0.5	18
	2-(2'-Carboxy-3'-chlorophenyl)perimidine	0.51	0.5	20

The absence of compound VI, and also the approximate simultaneity of the appearance and disappearance of compounds III and IV, of which compound IV is the more reactive, shows that the reaction does not take place by route A.

The fact that the phthaloperinone VIII does not appear in the reaction mixture immediately after the formation of naphthalene-1, 8-diamine (IV) and also the clear detection of compound IX, shows that the reaction takes place not by Scheme B but by Scheme C. The reaction of naphthalene-1, 8-diamine with phthalic anhydride, leading to compound IX [1], also shows the correctness of Scheme C. The formation of 2-methylperimidine (V) is the result of a side reaction of naphthalene-1, 8-diamine with acetic acid.

Thus, on the basis of the results obtained, it may be concluded that the formation of the phthaloperinone VIII takes place by the following stages: reduction of 1, 8-dinitronaphthalene (II) to 1-amino-8-nitronaphthalene (III), further reduction to naphthalene-1, 8-diamine (V), acylation of the latter with phthalic anhydride to form 2-(2'-carboxyphenyl)perimidine (IX), and dehydration to the phthaloperinone VIII.

The reaction takes place similarly in the case of 3-chlorophthalic anhydride and 1, 8-dinitronaphthalene (see table). The mechanism found is probably a general one for this type of transformation.

EXPERIMENTAL

Preparation of perinones from 1, 8-dinitronaphthalene. A mixture of 2.18 g (0.01 mole) of 1, 8-dinitronaphthalene, 1.48 g (0.01 mole) of phthalic anhydride (or 1.82 g (0.01 mole) of 3-chlorophthalic anhydride), 3.36 g (0.06 mole) of iron powder, and 80 ml of glacial acetic acid was heated at 80 ± 0.5° C with stirring. Samples of the reaction mixture were taken every 30 min and deposited on type "M" chromatographic paper impregnated with a 10% solution of 1-bromonaphthalene in ethanol simultaneously with the deposition of compounds II–VI, VIII, and IX (eluent 60% acetic acid). In UV light the phthaloperinone VIII was orange and the 11-chlorophthaloperinone VIII was red, while all the other compounds formed dark spots. When the chromatogram was treated with iodine, naphthalene-1, 8-diamine (IV) gave a dark blue spot, 2-methylperimidine (V) a dark green spot, and all the others brown spots. There were no unidentified spots on the chromatograms. The chromatographic data are given in the table. If the perinone-preparation reaction was carried out in boiling glacial acetic acid, the reaction was complete in 6–8 hr. The yields of the perinones amounted to 95–98%.

1-Amino-8-nitronaphthalene. A solution of 2 g of unpurified product obtained by Krasovitskii's method in 20 ml of benzene was passed through a 20 × 200 mm column of alumina, the first orange fraction being collected. After evaporation of the benzene, red crystals with mp 99.2–99.4° C were obtained.

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