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RESEARCHES ON ANTHRAPYRIDONES

I. Reaction of Anthrapyridone Derivatives with Phosphorus Pentachloride

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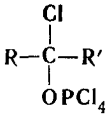
N-methylanthrapyridone (3-methyl-7H-dibenz [f, ij] isoquinolin-2, 7-dione) reacts with phosphorus pentachloride at 180° to give 2-chloroanthrapyridine (2-chloro-7H-dibenz [f, ij] isoquinolin-7-one), while at 130° C it forms an addition compound assumed to have the structure 2-tetrachlorophosphoxy-3-methyl-7-oxo-7H-dibenz [f, ij] isoquinolinium chloride. With primary amines the latter readily gives the corresponding 2-imines of anthrapyridone.

It is known that anthrapyridone (7H-dibenz [f, ij] isoquinolin-2, 7-diones) (I) and phosphorus pentachloride give 2-chloro-7H-dibenz [f, ij]-7-one (II) [1]. We have now shown that formation of II is observed under milder conditions, and in up to 80% yield, by the reaction of I with phosphorus oxychloride. It has also been shown that N-methylanthrapyridone (3-methyl-7H-dibenz [f, ij] isoquinolin-2, 7-dione) (III) and phosphorus pentachloride at 180° C give the same compound II. Quinoline derivatives behave similarly. 2-chloroquinolines can be obtained by treating quinol-2-ones with phosphorus oxychloride or pentachloride, and by reaction of N-methylquinol-2-ones with phosphorus pentachloride [2, 3, 4]. The latter reaction proceeds under more drastic conditions and is accompanied by demethylation of N-methylquinol-2-ones.

There are various views regarding the mechanism of the reaction of phosphorus pentachloride with carbonyl compounds. Many authors consider that the primary product of reaction of phosphorus pentachloride with ketones is a type A adduct. In a recent paper Newman [5] adduces indirect evidence for the formation of such an adduct. Theilacker and Bolsing [6] isolated the product of addition of phosphorus pentachloride to an o, o'-dialkyl-substituted benzophenone, with simultaneous chlorination of the benzene ring. On the other hand, papers by A. V. Kirsanov and coworkers [7, 8] show conclusively that when amides of carboxylic acids react with phosphorus pentachloride, the latter adds not to the carbonyl oxygen, but to the nitrogen, giving trichlorophosphoazoacyls.

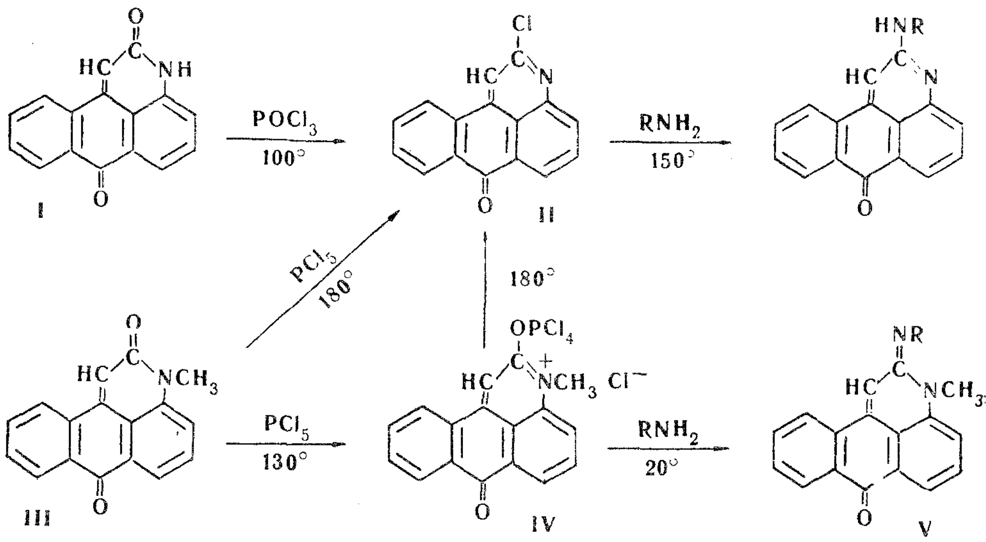


$\mathrm{R{-}}\overset{\mathrm{Cl}}{\underset{\mathrm{OPCl_4}}{\mathrm{C}}}\mathrm{{-}R'}$

A

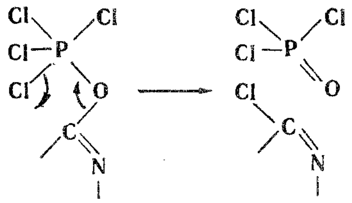
We noted that reaction of phosphorus pentachloride with the N-methyl-anthrapyridone III begins, not at 180° C, but at much lower temperatures. Working in chlorobenzene at 130° C, there can be isolated a crystalline compound whose analysis corresponds to an addition product between one molecule of phosphorus pentachloride and one molecule of III. The reaction takes place to give a yield close to the theoretical, without evolution of hydrogen chloride or formation of phosphorus oxychloride. Compound IV is a comparatively stable substance, which slowly hydrolyzes in air with evolution of hydrogen chloride. Compound IV dissolves when heated with water, then the starting N-methyl-anthrapyridine III quickly separates. On heating with dry trichlorobenzene, compound IV decomposes with formation of chloroanthrapyridine II. Compound IV very readily reacts with primary amines to give red crystalline compounds (V), which are not identical with the product of reaction of the same amines with the chloroanthrapyridine II. Analytical data for V correspond to N-methylanthrapyridon-2-imines. The structure of these imines was demonstrated by retrosynthesizing one, 2-(p-tolylimino)-3-methyl-7H-dibenz [f, ij] isoquinolin-7-one (Va). For that purpose, the 2-chloroanthrapyridine II was methylated with dimethylsulfate, and the resultant 2-chloro-3-methyl-7-oxodibenz [f, ij]-isoquinolinium methylsulfate was treated with p-toluidine. The two compounds were identical.

From the properties and transformations of compound IV it can be assumed that it is 2-tetrachlorophosphoxy-3-methyl-7-oxo-7H-dibenz [f, ij] isoquinolinium chloride. This structure is in good accord with such properties as solubility in water and relative stability of IV, and this structure is close to that put forward by Newman for products of addition of phosphorus pentachloride and carbonyl compounds. The positive charge in the pyridine ring stabilizes the



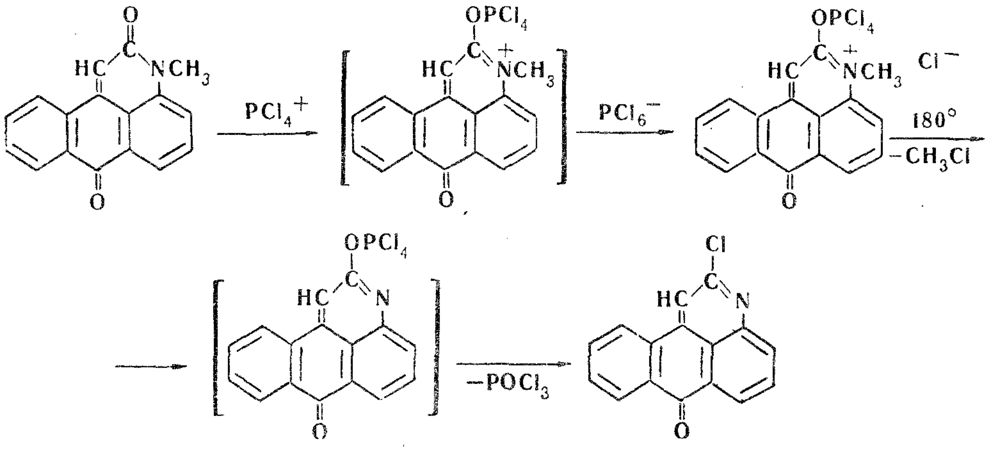
Va $R=o\text{-}C_6H_4CH_3$; Vb $R=C_6H_5$; Vc $R=H$; Vd $R=CH_2CH_2OH$

C—O bond. Change of the nitrogen atom from the quadruply charged to the trivalent state must be ascribed to splitting of a C—O bond according to a cyclic process:



Actually, warming IV with organic bases such as triethylamine gives the chloroanthrapyridine II, where the salt IV passing over into free base, quickly splits off phosphorus oxychloride.

It can be assumed that the reaction of phosphorus pentachloride with N-methylanthrapyridone proceeds thus:



Experimental

2-Tetrachlorophosphoxy-3-methyl-7-oxo-7H-dibenz [f, ij] isoquinolinium chloride (IV). 4.0 g (0.0153 mole) N-methylanthrapyridone (III) was added to 5 g (0.024 mole) PCl_5 dissolved in 80 ml dry chlorobenzene at 90° C, the temperature raised to 130° C, and the mixture stirred for 15 min. Under a microscope it could be seen that needles of III changed to plates and rhombs of addition product IV; a sample of the product, mixed with water, dissolved completely on heating. The products were cooled to 80° C, the lemon-yellow precipitate filtered off, washed with chlorobenzene to remove excess PCl_5, then with CCl_4, and dried in a vacuum-desiccator. Yield 7.20 g (100%). Found: Cl 37.22; 36.87; N 3.03, 3.33; P 6.97, 7.01%. Calculated for $C_{17}H_{11}Cl_5NO_2P$: Cl 37.71; N 2.98; P 6.59%.

On heating above 150° C the compound decomposed. On heating with water it readily dissolved, but from the hot solution the initial III was recovered, mp 267.2–268.0°. Undepressed mixed mp with the starting N-methylanthrapyridone. The literature [9] gives mp 267–268° C.

2-Chloro-7H-dibenz [f, ij] isoquinolin-7-one (II). a) 1.00 g anthrapyridone I was treated with 5 ml distilled $POCl_3$ at 90–100° C for 3 hr. After cooling the solution was poured into ice-water, the precipitate which formed filtered off, washed with hot water, and dried. Yield 0.86 g (80%), yellow needles (ex xylene), mp 257.5–260.0° C. The literature gives mp 260° [1], and 255° [9].

b) 1.00 g N-methylanthrapyridone III and 1.2 g PCl_5 were heated together for 8 hr at 170° in 15 ml dry trichlorobenzene, then the solvent distilled off under reduced pressure. The residue was recrystallized from p-xylene, using active charcoal, to give 0.43 g (44%) II, mp 257.3–258° C, identical with that prepared by method a. Found: Cl 13.67, 13.57; N 5.51, 5.62%. Calculated for $C_{16}H_8ClNO$: Cl 13.35; N 5.28%.

c) 0.5 g IV in 5 ml dry trichlorobenzene was heated at 170–175° C for 5 hr. The insoluble material gradually dissolved. 0.26 g II mp 256.0–257.0° was isolated from the reaction products. Undepressed mixed mp with a preparation obtained by method a.

2-(p-Tolylimino)-3-methyl-7H-dibenz [f, ij] isoquinolin-7-one (Va). a) 0.5 g IV was treated in the cold with a solution of 5 g p-toluidine in 12 ml $CHCl_3$; the dark red mixture was poured into dilute HCl, the $CHCl_3$ distilled off, the precipitate filtered off, and washed with warm dilute ammonia solution, to give 0.37 g (99%) p-tolylimino derivative. Purification by chromatography, in toluene solution, on aluminum oxide, followed by recrystallization from toluene, gave 0.19 g pure Va, mp 200.4–201.0° C, λ_{max} 355, 370, 505 mμ. Found: C 82.20, 82.46; H 5.22, 5.41; N 8.11, 8.07%. Calculated for $C_{24}H_{18}N_2O$: C 82.25; H 5.18; N 7.99%.

b) 0.50 g chloroanthrapyridine II was heated with excess Me_2SO_4 at 140°C, the products diluted with benzene, the precipitate filtered off, washed with benzene, and dried, yield of 2-chloro-3-methyl-7-oxo-7H-dibenz [f, ij] isoquinolinium chloride, 0.58 g. This latter was treated at 80° C with a solution of p-toluidine in $CHCl_3$, and the products worked up in the way described for preparation of Va by method a, to give 0.12 g Va, mp 199.3–200.6° C. Undepressed mixed mp with specimens obtained by other methods.

2-Phenylimino-3-methyl-7H-dibenz [f, ij] isoquinolin-7-one (Vb). 0.50 g IV was dissolved in the cold in 5 ml aniline. The reaction was accompanied by evolution of heat. The red solution formed was poured into excess dilute HCl, the yellow precipitate filtered off, boiled some minutes with 5% ammonia solution, when its color changed to dark red, filtered off, washed with water, and dried, to give 0.32 g (89%). The material was purified by chromatographing in $CHCl_3$ solution, on aluminum oxide, mp 213.2–214.4° C (ex EtOH), red needles. Found: C 81.72, 81.59; H 5.05, 4.87; N 8.13, 7.95%. Calculated for $C_{23}H_{16}N_2O$: C 82.12; H 4.79; N 8.32%.

2-Imino-3-methyl-7H-dibenz [f, ij] insoquinolin-7-one (Vc). 1.00 g IV was treated at 20° with ammonia solution (24%), the orange precipitate filtered off, washed with water, dissolved in 2% HCl, insoluble impurities filtered off, and the solution made alkaline with 0.5 N NaOH solution. The flocculent precipitate was filtered off, washed with water, and dried, yield 0.49 g (88%), mp 271.6–273.5° C (decomp, ex EtOH), λ_{max} 340, 455 mμ. Found: C 77.77, 77.93; H 4.74, 4.67; N 10.13, 10.30%. Calculated for $C_{17}H_{12}N_2O$: C 78.44; H 4.64; N 10.75%

2-(β-Hydroxyethylimino)-3-methyl-7H-dibenz [f, ij] isoquinolin-7-one (Vd). IV was treated in the cold with ethanolamine, and after purification by chromatography, a 78% yield of compound was obtained, mp 217.6–220° C (ex toluene). Found: C 75.35, 75.55; H 5.33, 5.47; N 9.86, 9.64%. Calculated for $C_{19}H_{16}N_2O_2$: C 74.98; H 5.27; N 9.20%.

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