STUDIES IN THE FIELD OF ANTHRAPYRIDONE

V. Anthrapyridinium* Compounds and Their Reaction with Compounds Containing Active Methylene Groups**

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A series of cyanines has been obtained by the reaction of 3-methyl-2-methylthioanthrapyridinium methosulfate (V) with compounds containing active methylene groups. Compound V was synthesized from N-methylanthrapyridone by the action of phosphorus oxychloride, treatment of the resulting 2-dichlorophosphonyloxy-3-methylanthrapyridinium chloride with thiourea, and the reaction of the Nmethylanthrapyridine-2-thione with dimethyl sulfate.

In the first communication, we described the reaction of N-methylanthrapyridone (I) with phosphorus pentachloride, leading to the formation of 2-tetrachlorophosphoranyloxy-N-methylanthrapyridinium chloride (II) and noted its high reactivity, especially with respect to amines [1].

It has been found that, like phosphorus pentachloride, phosphorus oxychloride reacts with N-methylanthrapyridone (I) at 90–100° C forming an addition product for which, on the basis of its properties, we assume the structure of 2-dichlorophosphonyloxy-3methylanthrapyridinium chloride (III). A similar compound has recently been described in the quinoline series [2]. Compound III, like II, readily forms the corresponding anthrapyridone 2-imines on reaction with primary amines. The chloride III readily reacts with thiourea in aqueous solution, forming the thio analog of N-methylanthrapyridone (IV), which, on treatment with dimethyl sulfate, gives N-methyl-2methylthioanthrapyridinium methosulfate (V).



It is known that quaternary salts of nitrogen-containing heterocyclic bases with groups capable of being split off in the form of an anion (chlorine, methylthio, etc.) in the ortho and para positions react with compounds containing active methylene groups to form cyanine dyes [3-5]. The anthrapyridinium compounds II, III, and V that we have synthesized also react with methylene-containing compounds. The process takes place most smoothly with the methylthic compound V: the methyl mercaptan liberated volatilizes off, and the methyl hydrogen sulfate is bound by the addition of triethylamine.



To synthesize the cyanines we used the ethyl esters of acetoacetic, benzoylacetic, cyanoacetic, and malonic acids and also 3-hydroxythionaphthene and 4,5-benzo-3-hydroxythionaphthene. The substances obtained are colored compounds, red to green according to the nature of the methylene component. In the visible region of the spectrum, they each exhibit a broad absorption band which is probably due to the complexity of the chromophoric system and the possibility of cis-trans isomerism relative to the double bond. In the final dyes, a shift of the main absorption band in the long-wave direction on passing from one methionine component to another is found in the sequence malonic ester < cyanoacetic ester < benzoylacetic ester < acetoacetic ester < hydroxythionaphthene < benzohydroxythionaphthene.

EXPERIMENTAL (L. D. Zil'berg took part in the work).

2-Dichlorophosphonyloxy-3-methyl-7-oxo-7H-dibenz[f, ij]isoquinolinium chloride (III). A mixture of 26.1 g (0.1 mole) of II, 40 ml (0.44 mole) of phosphorus oxychloride, and 260 ml of dry toluene was stirred at $90-100^{\circ}$ C for 3 hr, by which time the sample of the solid material taken from the reaction mixture was soluble in water. After cooling, the solid matter was filtered off and was washed with dry petroleum ether to give 39.4 g (95%) of III in the form of a yellow microcrystalline powder readily soluble in water and insoluble in benzene, chloroform, and ether. Found, %: Cl 26.22, 26.01. Calculated for $C_{17}H_{11}Cl_{3}NO_{3}P$, %: Cl 25.65.

3-Methyl-7-oxo-7H-dibenz[f, ij]isoquinoline-2-thione (IV). At $10-15^{\circ}$ C. 15 g (0.036 nnole) of III was dissolved in 500 ml of water. and a solution of 10 g (0.13 mole) of thiourea in 150 ml of water was added. A red precipitate immediately appeared. After 30 minutes' standing with periodic stirring, the precipitate was filtered off and was washed repeatedly with water and dried. Yield 9.8 g (98%). After recrystallization from chlorobenzene, 6.6 g of IV was obtained in the form of red-orange plates, mp 264-265.5° C, λ_{max} 295, 355, 370 and 475 nm, log ε 4.45, 4.17, 4.17, and 4.08. Found, %: C 73.65;

^{*}On the nomenclature used in this paper, see the note to the preceding paper [Translator's note]. **For part IV, see [6].

Com - pound	Name	Мр, ⁰С	λ_{\max} , nm (log ε)	Empirical formula	Found, %			Calculated, %			Vield of
					С	н	N	с	н	N	, 1010, 70
VIa	2-(Acetylethoxy- carbonyl)methyl- ene-3-methyl- 7H-dibenz[f,ij]- isoquinolin-7-one	239.6— 241.0	340 (4.19) 540 (4.09)	C ₂₃ H ₁₉ NO ₄	74.23 74.18	5,23 5,25	4.08 4,21	73.98	5.13	3.75	76.4
VIb	2-(Benzoylethoxy- carbonyl)meth- ylene-3-methyl- 7H-dibenz[f,ij]- isoquinolin-7- one	227.2— 228.4	355 (4.26) 515 (4.23)	C ₂₈ H ₂₁ NO ₄	79.02 78.92	5.09 5.04	3.42 3.20	80.35	5.05	3.34	52.5
VIc	2-Diethoxycar- bonylmethylene- 3-methyl-7H- dibenz[f, ij]- isoquinolin- 7-one	167.6— 168.4	315 (4.27) 355 (4.13) 495 (4.14)	C ₂₄ H ₂₁ NO ₅	71.95 72.09	4.99 4.82	3.02 3.31	71.45	5.25	3.47	70
VId	2-(Cyanoethoxy- carbony1)meth- ylene-3-methy1- 7H-dibenz[f,ij]- isoquinolin-7- one	215.4 <i></i> 216.6	310 (4.37) 360 (4.18) 500 (4.25)	$C_{22}H_{16}N_2O_3$	74.96 75.08	4.66 4,72	7.87 7.66	74.14	4.52	7.86	90
VIIa	2-(3'Hydroxythio- naphthylidene)-3- methyl-7H-dibenz [f, ij]isoquinolin- 7-one	290.7— 292.0	380 (4.33) 620 (4.22)	C ₂₅ H ₁₅ NO ₂ Sa			3.61 3.72			3.56	96.5
VIIb	2-(4',5'-Benzo- 3'-hydroxythio- naphthylidene)- 3-methyl-7H- dibenz[f, ij]iso- quinolin-7-one	258.0— 259.0	335 (4.10) 405 (4.30) 645 (4.23)	C ₂₉ H ₁₇ NO ₂ Sb	78.11 78.32	4.05 4.09		78,53	3.87		66

Cyanines Obtained from 3-Methyl-2-methylthioanthrapyridinium Methosulfate

^aFound, %: S 7.92, 7.99. Calculated, %: S 8.15%. ^bFound, %: S 7.02, 6.98. Calculated, %: S 7.23.

CHEMISTRY OF HETEROCYCLIC COMPOUNDS

73.96; H 3.98; 3.99; S 10.71, 11.01%. Calculated for $C_{17}H_{11}NOS,$ %: C 73.62; H 4.00; S 11.56%.

3-Methyl-2-methylthio-7-oxo-7H-dibenz[f, ij]isoquinolinium methosulfate (V). A mixture of 6.92 g (0.025 mole) of IV and 3.4 g (0.027 mole) of dimethyl sulfate was boiled in 200 ml of dry toluene for 1 hr to 1 hr 30 min. After cooling, the bright yellow precipitate was filtered off, washed three times in toluene (50 ml), and dried. The yield of V was 9.47 g (94%), mp above 200° C (decomp.), readily soluble in water, insoluble in benzene and ether. Found, %: N 3.52, 3.61; S 16.05, 16.32%. Calculated for $C_{10}H_{17}NO_5S_2$, %: N 3.47; S 15.89%.

2-(Cyanoethoxycarbonyl)methylene-3-methyl-7-oxo-7H-dibenz-[f, ij]isoquinoline (VId). A mixture of 0.4 g (~0.001 mole) of V, 0.7 ml (0.0055 mole) of cyanoacetic ester, and 0.1 g (0.001 mole) of triethylamine was heated to 50° C in 30 min and was stirred at this temperature for 15 min. The precipitate was filtered off and washed with 30 ml of methanol to give 0.32 g of VId (90%), mp 215.4-216.6° C (from chlorobenzene). The spectral and analytical data are given in the table.

The cyanines VI and VII, the properties of which are given in the table, were obtained similarly.

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