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INTRAMOLECULAR CYCLIZATION OF 9,10-ANTHRAQUINONES PROMOTED BY REACTION WITH HALOGENOPHOSPHORANES

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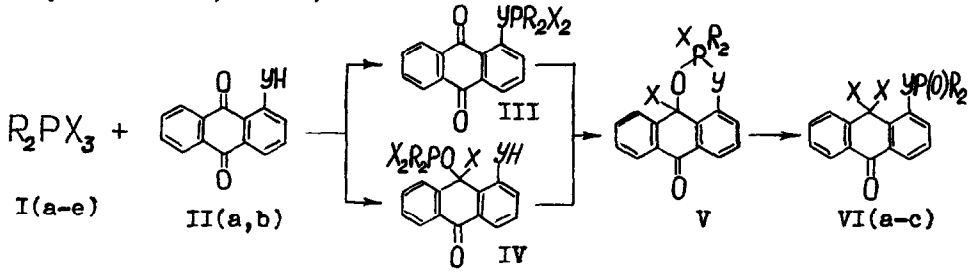
The results of the research of an unknown reaction of halogenophosphoranes (Ia-e) with peri-oxy(amino)-9,10-anthraquinones leading to the formation of anthrones (VIa-e,XIII) and tetrahydroanthracenes (XIa,b) are reported. The scheme of reaction includes the formation of phosphabenzanthrone (V) and anthraquinone (III) which was fixed by a low temperature ^{31}P NMR spectroscopy. The driving force of discovered reaction of anthraquinone cyclization is explained by specific character of transference of electronic influence from substituents to a carbonyl group contained in anthraquinones. Certain properties of products formed having an unusual structure from the viewpoint of the chemistry of anthraquinones are described.

Introduction.

As the continuation of works[1-4] dedicated to the studies of the interaction of phosphorus organic compounds with quinones, the reactions of halogenophosphoranes with oxy- and amino-anthraquinones being of great importance to the chemical science and industry[5] are investigated in the present paper.

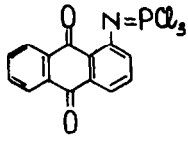
Results.

In the reaction of phosphorus pentachloride (Ia) with oxyanthraquinone (IIa), phosphorylated anthrone (VIa) was obtained instead of expected phosphorane anthraquinone (III, X=R=Cl, Y=O).



	Ia	Ib	Ic	Id	Ie	IIa	IIb	VIa	VIb	VIc
X	Cl	Cl	Cl	Cl	Br			Cl	Cl	Cl
Y						O	NH	O	NH	O
R	Cl	t	Ph	OC_6H_4O	Br			Cl	Cl	t

In the reaction of PCl_5 with aminoanthraquinone (IIb), anthrone (VIb) was obtained that was erraneously defined as phosphazoanthraquinone (VII) by Shermolovich and co-workers[6]. In the present paper the structure of (VIb) was



VII

verified by X-ray structural analysis that showed a tricyclic fragment to be almost planar in this molecule (the dihedral angle between benzene ring planes is 5.3°). The molecular geometry of (VIb) is given in Fig.1 and in Table 1.

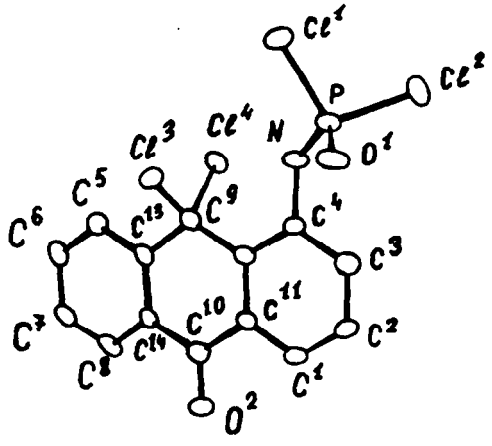


Fig.1. Molecular geometry of (VIb).

Table 1. Selected geometrical parameters of the molecule (VIb).

	Bond	Lengths d(Å)	
P - Cl (1)	1.986(1)	N - C(4)	1.421(4)
P - Cl (2)	2.002(1)	C(9)-C(12)	1.507(5)
P - O (1)	1.456(3)	C(9)-C(13)	1.518(5)
P - N	1.625(3)	C(10)-C(11)	1.489(5)
Cl(3)-C(9)	1.827(3)	C(10)-C(14)	1.473(5)
Cl(4)-C(9)	1.807(3)	C(11)-C(12)	1.413(5)
O(2)-C(10)	1.223(4)	C(13)-C(14)	1.392(5)
	Bond	Angles (°)	
Cl(1)PCl(2)	102.12(6)	Cl(3)C(9)Cl(12)	109.0(2)

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Bond		Angles (°)	
Cl(1)PO(1)	113.5(1)	Cl(3)C(9)Cl(13)	107.8(2)
Cl(1)PN	104.7(1)	Cl(4)C(9)C(12)	110.0(3)
Cl(2)PO(1)	111.5(1)	Cl(4)C(9)C(13)	106.0(2)
Cl(2)PN	108.7(1)	C(12)C(9)C(13)	117.2(3)
O(1)PN	115.3(2)	O(2)C(10)C(11)	120.5(3)
PNC(4)	123.6(2)	O(2)C(10)C(14)	121.2(4)
Cl(3)C(9)Cl(4)	106.2(2)	C(11)C(10)C(14)	118.3(3)

The bond lengths of the cyclic fragment are close to their average values of the corresponding type. The C^9-Cl^3 and C^9-Cl^4 bond lengths are significantly different (1.827(4) and 1.807(3) Å, respectively) and exceed the average C-Cl value observed in X_2CCl_2 fragments[7]. Phosphorus atom has a distorted tetrahedral coordination. Large difference between the P-Cl bond length in this molecule can be explained by the generalized anomeric effect. In Fig.2 showing Newman projection along the N-P bond, it can be seen that the orientation of the P-Cl^1 bond is much more favourable for n-π^* interaction between the nitrogen lone electron pair and antibonding P-Cl orbital than that of the P-Cl^2 bond.

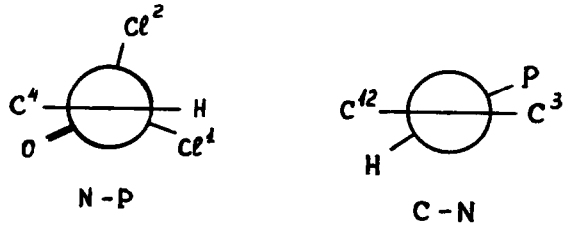


Fig.2. Newman projection along the N-P and C-N bonds.

The P-N-C^4-C^3 torsional angle being equal to -34.3°, the interaction between the nitrogen lone electron pair and the π-system of benzene ring is diminished. In the crystal, molecules (VIb) form infinite zigzag chains along the Z axis due to N-H...O^{1} hydrogen bonds with the following parameters: N...$O^{1'}$ (x, 1/2 - y, 1/2 + z) 2.896 Å; N-H 0.84 Å; H...$O^{1'}$ 2.18Å; N-H...$O^{1'}$ 143°.

Besides PCl_5, the reactions of Et_2PCl_3, Ph_2PCl_3, pyrocatecholtrichlorophosphorane, PBr_5 with anthraquinones (IIa,b) have been studied. In all

cases the formation of products having an unusual structure (VIa-c,XX,XXII) (Tables 2-4) can be observed. Two real reaction schemes of product formation could be assumed. The first scheme involves initial substitution of a hydrogen atom of an oxy- or amino-group by a phosphorane fragment with the formation of anthraquinone (III) and the subsequent intramolecular cyclization with the participation of C=O bond and the formation of phosphabenzanthrone (V) that is stabilized into anthrone (VIa-c). According to another scheme, the opening of a carbonyl group already takes place at the beginning of the reaction with the formation of anthrone (IV)undergoing intramolecular substitution leading to phosphabenzanthrone (V) from which a final product (VIa-c) is obtained. Within the frameworks of the schemes presented, the processes of an intramolecular character are not excluded; in particular, (III) → (VIa-c) or (IV) → (VIa,b) transformations proceed, probably, during the reaction of (III) or (IV) with phosphorus pentachloride.

In order to make a choice of a particular scheme, model reactions of halogenophosphoranes and 9,10-anthraquinones have been performed. It has been found out that phosphorus pentachloride and other halogenophosphoranes do not react with unsubstituted 9,10-anthraquinone, 1-methoxy- and 1-methylamino-9,10-anthraquinones. On the basis of this fact, it can be concluded that halogenophosphoranes do not open a carbonyl group of the above mentioned anthraquinones in spite of the absence of hindrances, on the contrary, substituents (H, OMe, NHMe) have been selected so as to completely reproduce electron and steric structure of anthraquinones (IIa,b). Therefore, at the first stage of the reaction halogenophosphoranes, probably, do not interact with a carbonyl group of anthraquinones (IIa,b) and do not form anthrones (IV). Besides, it has been found out that phosphorus pentachloride easily reacts with 2,6-dioxy- and 2-amino-9,10-anthraquinones with formation of condensation products (VII,IX) obtained from the reaction mixture in the form of anthraquinones (VIII,X).

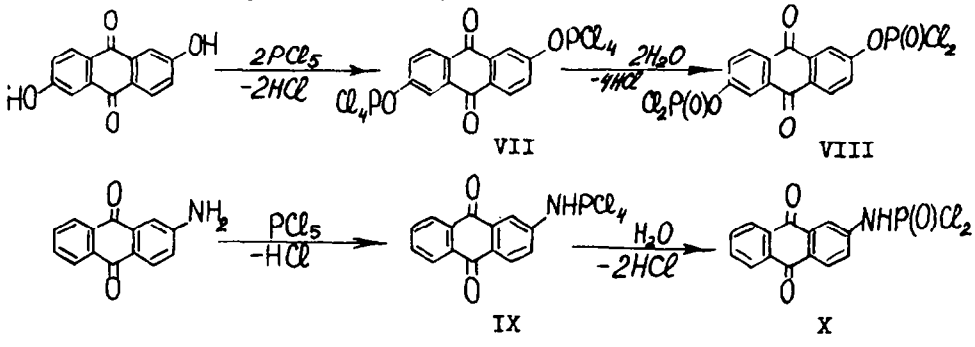


Table 2. Methods of Synthesis, Physico-Chemical Constants and Elemental Analysis Data of the Compounds.

Compound N	Method of synthesis	Reaction time, hours	Yield %	Melting point, °C	Amount in % *					Formula
					C	H	Cl, Br	N	P	
VI a	A	0.5	94	150 (benzene-heptane)	42.23 / 42.42	2.08 / 1.77	34.08 / 35.86		8.06 / 7.83	$C_{14}H_7Cl_4O_3P$
VI b	A E	0.5 1.5	98 92	153 (hexane)	42.12 / 42.53	1.93 / 2.03	35.10 / 35.94	3.23 / 3.54	7.68 / 7.85	$C_{14}H_8Cl_4NO_2P$
Vi c	A	0.5	30	70 (benzene-heptane)	56.28 / 56.40	3.90 / 4.44	17.64 / 18.53		8.81 / 8.09	$C_{18}H_{17}Cl_2O_3P$
VIII	A	1	80	177 (chloroform)	34.77 / 35.44	1.34 / 1.26	29.08 / 29.96		13.61 / 13.08	$C_{14}H_6Cl_4O_6P_2$
X	A	1	75	205 (heptane)	49.19 / 49.41	3.07 / 2.35	19.95 / 20.88	3.50 / 4.12	10.13 / 9.12	$C_{14}H_8Cl_2NO_3P$
XI a	B	1.5	85	152 (acetone-benzene)	28.84 / 28.76	1.21 / 1.03	48.23 / 48.63		11.06 / 10.61	$C_{14}H_8Cl_8N_2O_2P_2$
XI b	B	1.5	82	150 (acetone-benzene)	29.31 / 28.87	1.46 / 1.37	47.94 / 48.80	4.45 / 4.81	10.40 / 10.65	$C_{14}H_8Cl_8N_2O_2P_2$
XIII	C	1.5	86	148 (benzene-heptane)	31.89 / 31.76	1.59 / 1.13	39.39 / 40.26		12.63 / 11.72	$C_{14}H_6Cl_6O_5P_2$
XV	C	0.5	80	142 (benzene-heptane)	36.01 / 35.44	0.98 / 1.26	29.69 / 29.96		13.74 / 13.08	$C_{14}H_6Cl_4O_6P_2$
XVI	C	1	68	179 (hexane)	32.71 / 33.01	1.33 / 1.18	41.81 / 41.85	5.54 / 5.50	12.76 / 12.18	$C_{14}H_6Cl_6N_2O_2P_2$

- continued -

Compound N	Method of synthesis	Reaction time, hours	Yield %	Melting point, °C	Amount in % *					Formula
					C	H	Cl,Br	N	P	
XVII	D	0.5	85	132 (benzene-heptane)	70.12 / 69.28	3.02 / 2.89	14.12 / 14.64			$C_{14}H_7ClO_2$
XVIII	D E	0.25 2	95 98	130 (heptane)	47.15 / 46.86	2.06 / 1.95	29.03 / 29.71	3.87 / 3.91	8.50 / 8.65	$C_{14}H_7Cl_3NO_2P$
XX	A	0.5	80	121 (benzene)	71.10 / 70.67	4.07 / 3.85	7.86 / 8.04	3.31 / 3.17	7.0 / 7.02	$C_{26}H_{17}ClNO_2P$
XXII	A	1	88	146 (benzene-heptane)	60.15 / 60.68	3.07 / 2.78	8.36 / 8.98	3.08 / 3.54	7.93 / 7.84	$C_{20}H_{11}ClNO_4P$
XXIV	A	1	80	155 (benzene-heptane)	33.96 / 34.15	1.74 / 1.42	47.81 / 48.78	3.04 / 2.85	6.5 / 6.30	$C_{14}H_7Br_3NO_2P$
XXV a	G	2	70	149 (benzene-heptane)	56.85 / 57.46	3.67 / 4.51		4.12 / 3.94	8.20 / 8.73	$C_{17}H_{16}NO_2P$
XXV b	G	2	65	162 (benzene-heptane)	62.54 / 62.02	6.39 / 5.68		3.17 / 3.62	8.35 / 8.01	$C_{17}H_{16}NO_5P$
XXV c	G	2	76	147 (benzene-heptane)	64.09 / 64.34	6.39 / 6.53		3.76 / 3.26	17.01 / 7.23	$C_{23}H_{28}NO_5P$
XXV d	G	2	65	155 (benzene-heptane)	64.96 / 64.34	6.13 / 6.53		3.24 / 3.26	7.44 / 7.23	$C_{23}H_{28}NO_5P$
XXV e	G	2	55	156 (benzene-heptane)	65.81 / 66.24	8.12 / 7.22		3.49 / 2.47	7.55 / 6.58	$C_{26}H_{34}NO_5P$

- continued -

Compound N	Method of synthesis	Reaction time, hours	Yield %	Melting point, °C	Amount in % *					Formula
					C	H	Cl, Br	N	P	
XXVI	H I	2.5 2.5	80 69	205 (acetone)	72.07 73.00	4.36 4.37		10.86 10.64	5.81 5.89	$C_{32}H_{23}N_4O_2P$
XXVII	J	1	92	144 (o-xylene-heptane)	33.26 33.00	1.33 1.18	41.61 41.85	5.63 5.50	12.06 12.18	$C_{14}H_6Cl_6N_2O_2P_2$
XXVIII	K	2.5	60	146 (acetone-benzene)	70.47 70.92	4.70 4.73		13.15 13.24	3.93 3.78	$C_{50}H_{40}N_8O_2P_2$
XXIX	L	2	85	154 (benzene-heptane)	45.21 44.74	1.58 1.60	27.17 28.36		8.01 8.26	$C_{14}H_6Cl_3O_4P$
XXXI	M	2	50	133 (benzene-hexane)	46.79 47.58	4.67 4.41		7.03 6.17	14.09 13.66	$C_{18}H_{20}N_2O_8P_2$
XXXII	N	1.5	84	142 (benzene-heptane)	50.49 49.68	3.02 2.55	22.76 22.61		10.34 9.87	$C_{26}H_{16}Cl_4O_5P_2$
XXXVI	O	2.5	63	1.5415** (acetone-pentane)	55.70 55.68	5.91 5.80	16.37 16.47		6.86 7.19	$C_{20}H_{25}Cl_2O_4P$

Note: * above the line is the amount found, below the line is the amount calculated.

** Refractive index, n_D^{20}

Table 3. IR Spectral Data of the Compounds.

Compounds	IR spectrum, ν, cm^{-1}					
	NH	C=C, C=N, aromatic ring	C=O	P=O, anthraquinone ring	POC(PNC)	PCl (PBr)
1	2	3	4	5	6	7
VI a		1590, 1600	1680	1250, 1310	1040	500, 570, 625, 640
VI b	3240	1595	1675	1273, 1320	(1025)	530, 540, 582
VI c		1590	1675	1210, 1280, 1320	1045	
VIII		1610	1685	1230, 1270, 1320	1000, 1050	545, 580, 620
X	3210	1590	1680	1275, 1300, 1330	(1024)	510, 555, 600
XI a		1570, 1615		1250, 1300	1080	540, 555, 590
XI b	3175	1585, 1610		1270, 1300	(1040)	505, 520, 670
XIII		1575, 1590, 1605	1684	1250, 1300	1020, 1080	555, 590, 630
XV		1595	1680	1260, 1330	1040	570
XVI		1570, 1610	1670	1240, 1275	1040	530, 580, 595
XVII		1590	1690	1250, 1280, 1330		
XVIII		1595	1675	1280, 1320	1040	545, 575, 610
XX		1585, 1600	1675	1280, 1320	(1050)	
XXII		1580, 1600	1680	1240, 1285, 1320	950	
XXIV		1600	1685	1280, 1330	(965, 1020)	(480, 530)
XXV a		1590	1680	1280, 1320	1025	
XXV d		1585	1680	1280, 1320	1030	
XXV e		1590	1675	1275, 1330	1030	
XXVI	3100	1590, 1600, 1610		1280	(1030)	
XXVII		1545, 1625		1270, 1305	(1030)	545, 575
XXVIII	3120			1270, 1280	(1020, 1030)	
XXIX		1595	1675	1255, 1330	1025	550, 580, 610, 670

- continuation -

Compound N	IR spectrum, ν, cm^{-1}					
	NH	C=C, C=N, aromatic ring	C=O	P=O, anthraquinone ring	POC(PNC)	PCl (PBr)
XXXI	3200	1510, 1620	1670	1210, 1280, 1320	1040, 1075	
XXXII		1590	1680	1310, 1330	930	540, 568, 610, 625
XXXVI		1580	1620	1280	1050	565, 630

Table 4. NMR and Mass Spectral Data of the Compounds.

Compound N	^{31}P NMR spectrum δ, ppm	^{1}H NMR spectrum, δ ppm		Mass-spectrum, M/z, (relative intensity, %)
		NH, ($^{3}J_{PNH}$, Hz)	HC_{ap}, HC=	
VI a	4.3		8.18m, 7.83m	[M] $^{+}$394(9); [M-Cl] $^{+}$ 359(20); [M- 2Cl] $^{+}$ (15)
VI b	3.3	7.9d(25)	8.18m, 7.6m	[M+1] $^{+}$394(10); [M+1-Cl] $^{+}$358(50); [M-2Cl] $^{+}$344(10)
VI c	15		8.50m, 8.25m	[M] $^{+}$382(5); [M-Cl] $^{+}$ 347 (45)
VIII	0.6		7.95m	[M+1] $^{+}$472(5); [M+1-Cl] $^{+}$ 437 (19)
X	3.2	11.5d (30)	8.26m, 7.6m	[M] $^{+}$ 339(7); [M-HCl] $^{+}$303(15); [M-2Cl] $^{+}$269(20)
XI a	0.1			[M+3] $^{+}$583(6); [M+3-Cl] $^{+}$548(11); [M+3-2Cl] $^{+}$513(16)
XI b	6.0	10.3d(25)	7.6m, 6.45m	[M-HCl-2Cl] $^{+}$472(13); [M-HCl-3Cl] $^{+}$437(18)
XIII	0.8		8.2m, 7.7m	[M-2Cl] $^{+}$ 466(19)
XV				[M-2Cl] $^{+}$ 402(3); [M-4Cl] 332(12)
XVI	10.9			[M-Cl] $^{+}$ 436(10); [M-2Cl] $^{+}$ 401 (25)
XVII			8.14m, 7.80m	[M] $^{+}$242 (12)? [M-Cl] $^{+}$ 207(30)
XVIII	3.0		8.14m, 7.75m	[M+4] $^{+}$ 361(6); [M+4-Cl] $^{+}$ 322(16)
XXII	20			[M+1-Cl] $^{+}$ 407(11)

- continuation -

Compound N	^{31}P NMR spectrum δ, ppm	^{1}H NMR spectrum, δ, ppm: NH, ($^{3}J_{PNH}$, Hz)	HC_{ap}, HC=	Mass-spectrum, m/z, (relative intensity, %)
XXIV	1.2			
XXV a		MeO: 3.8d ($^{3}J_{POC}$ 15 Hz)	8.18m, 7.76m	$[M-CH_3O]^+$ 324(20)
XXV b		tO: 1.5T, 4.1m ($^{3}J_{POC}$ 15 Hz)	8.18m, 7.76m	$[M+1]^+$ 388(6); $[M+1-CH_3]^+$ 372(150); $[M+1-C_2H_5O]^+$ 342(10)
XXV c		PrO: 1.7m, 4.2m ($^{3}J_{POC}$ 15 Hz)	8.18m, 7.76m	$[M+1]^+$ 440(8); $[M+1-C_3H_7O]^+$ 381(16)
XXV d	1.3	iPrO: 1.6d, 3.9m ($^{3}J_{POC}$ 15 Hz)	8.18m, 7.76m	
XXVI	-6.5	9.5s	8.05m, 7.6m, 7.15m	$[M-NHPh]^+$ 417(14)
XXVII	4.9			$[M-HCl-2Cl]^+$ 400(8); $[M-2HCl-2Cl]^+$ 364 (10)
XXVIII	-6.0	9.7s	8.05m, 7.6m, 7.15m	
XXIX				$[M]^+$ 347(7); $[M-Cl]^+$ 339(25); $[M-2Cl]^+$ 304(15)
XXXI		8.2d(25)	8.2m, 7.6m	$[M+1]^+$ 450(14); $[M+1-CH_3O]^+$ 419(20)
XXXII				$[M]^+$ 610(13); $[M-Cl]^+$ 575(19)
XXXVI	2.5			$[M-Cl]^+$ 395(6); $[M-2Cl]^+$ 360 (56)

Comparing the result of the last reaction with previous data, the following conclusions can be made:

a) Oxy- or amino group is the most reactive center of substituted anthraquinones in the reactions with halogenophosphoranes.

b) Carbonyl group of 2-oxy(amino)-substituted anthraquinone does not participate in the reaction since an oxy(amino)-phosphorane fragment of molecules (VII,IX) is in the 2-position in which C=O group is not available for an intramolecular attack; at the same time, there exist favourable conditions for the intermolecular interaction which is not realized.

Thus, the most probable direction of the reaction of halogenophosphoranes with 1-oxy(amino)-9,10-anthraquinone is the initial formation of anthraquinone (III) with its subsequent conversion into phosphabenzanthrone (V) and later to anthrone (VI a-c).

In the investigations of the reaction of PCl_5 with anthraquinone (II b), by a low temperature ^{31}P NMR spectroscopy a singlet signal of anthraquinone (III, R=X=Cl, Y=NH) with a chemical shift of -42.9 ppm was recorded which is characteristic of the compounds of an acyclic pentacoordinated phosphorus atom (Fig.3.). The dynamics of the increase and decrease of the signal confirms the scheme according to which anthraquinone (III) is a reaction intermediate.

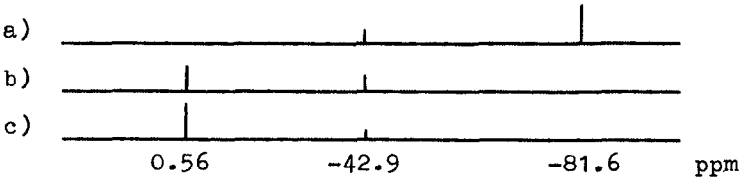
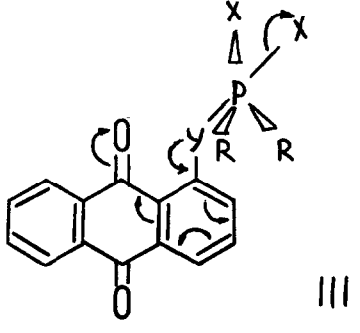


Fig.3. ^{31}P NMR spectrum of the reaction mixture of PCl_5 and anthraquinone (II b) at t=5°C upon mixing of reagents in a) 5 minutes, b) 30 minutes, c) 10 hours.

A matter of importance is the driving force of the transformations observed. At the first stage of the interaction, an energy-advantageous reaction of anthraquinone (III) and HCl formation takes place.



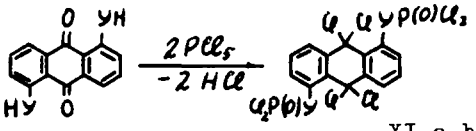
III

The second stage of the process is the isomerization of anthraquinone (III) into phosphabenzanthrone (V) which is caused by the simultaneous action of several factors:

- direct polar conjugation between 1-y substituent and 9-C=O-group resulting in the increase of electrophilicity of an oxygen atom in anthraquinone (III).
- presence of a Y heteroatom in the phosphorane fragment of tne molecule (III) resulting in the increase of nucleofugicity of an apical halogen X.
- possibility of bonding of oxygen and phosphorus atoms in anthraquinone (III) with the formation of a relatively stable 6-membered phosphabenzanthrone ring (V).

During the final,third stage of the reaction,phosphabenzanthrone (V) is transformed into anthrone (VI a-c) which is associated with the formation of a more stable phosphate structure (VIa-c)compared to phosphorane(V).

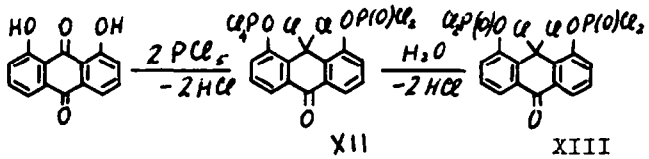
It was found out that in 1,5- and 1,8-disubstituted 9,10-anthraquinone series,intramolecular cyclization can also be observed.In the reactions of PCl_5 with 1,5-dioxy- and 1,5-diamino-9,10-anthraquinones,opening of both carbonyl groups of anthraquinones and the formation of phosphorylated tetrahydroanthracenes (XI a,b) are reported.



XI a,b

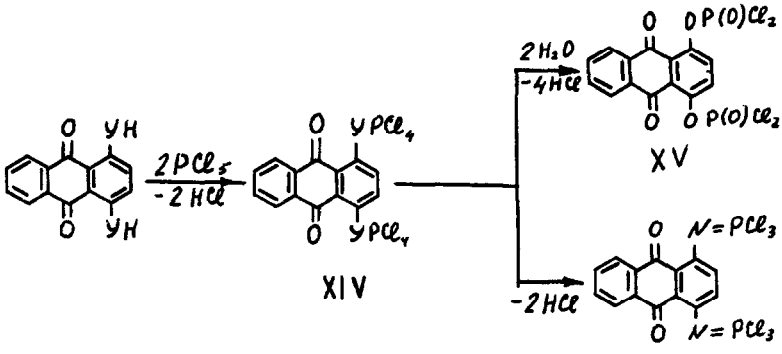
Y=O(a), NH(b).

The reaction of PCl_5 with 1,8-dioxy-9,10-anthraquinone via anthrone(XII) formation,leads to final anthrone (XIII).



XII XIII

PCl_5 and 1,4-dioxy- and 1,4-diamino-9,10-anthraquinones react in a different way.Intermediate anthraquinone (XV) is not isomerized in a similar way as anthraquinone (III,XII); instead,it is subjected to conventional hydrolysis or dehydrochlorination resulting in the formation of anthraquinones (XV,XVI),respectively.Such difference is probably associated with the decrease in the substituents' effect on the carbonyl group of 1,4-substituted 9,10-anthraquinones that can be explained[5] by the encounter of the oppositely directed effects of direct polar conjugation of two pairs of substituents: 1-XH,9-C=O and 4-XH,10-C=O,where X=O,NH.

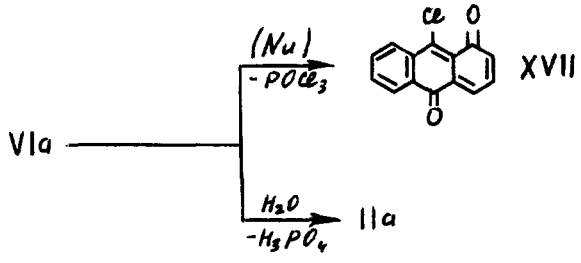


XIV XV XVI

Thus,during the interaction of halogenophosphoranes with substituted anthraquinones having peri-oxy(amino) groups (except 1,4-derivatives),intramolecular cyclization of intermediate compounds with the formation of anthrones (VI a-c,XIII) and tetrahydroanthracenes (XI a,b) takes place.

The products obtained (VI a-c,XI a,b,XIII,XIX,XXI) are the unknown anthracene derivatives,therefore,the investigation of their chemical properties is of particular interest.

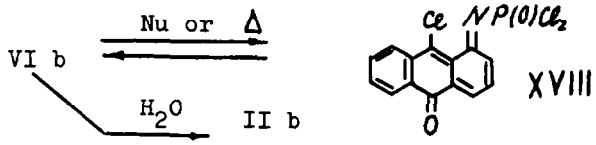
Under the influence of nucleophilic reagents (Nu),anthrone (VI a) is transformed into anthraquinone (XVII) and phosphorus oxychloride.Anthrone (VI a) hydrolysis results in the initial anthraquinone (II a).



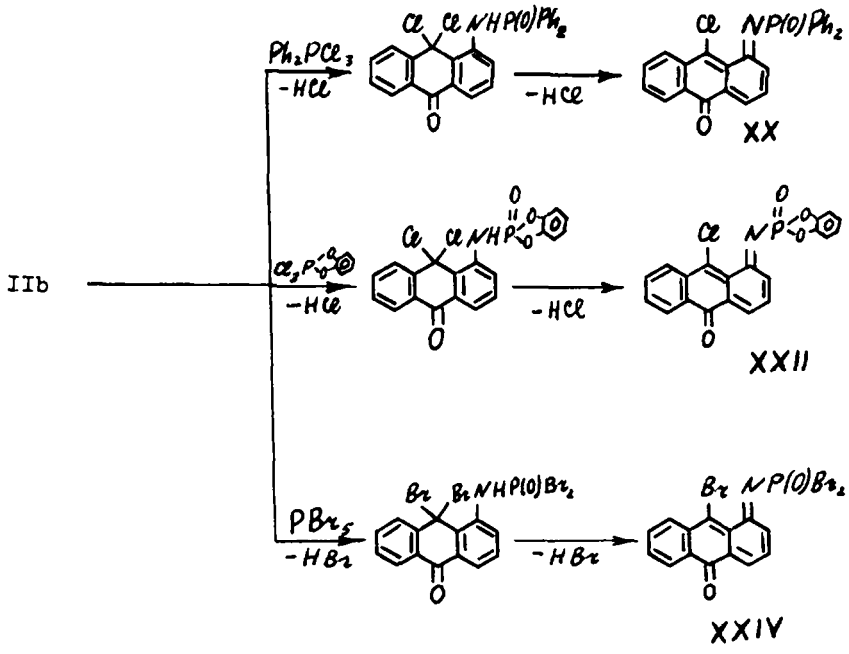
XVII

Nu is alcohols,amines,mercaptans

In the reactions of anthrone (VI b),as a rule,dehydrochlorination and formation of anaquinoneimine (XVIII) or its derivatives is reported.Similar result can be observed,for instance,in the thermolysis of anthrone (VI b) or in the reaction of the latter with nucleophiles.Upon the reaction of anaquinoneimine (XVIII) with HCl,anthrone (VI b) can be obtained. Anthrone (VI b) hydrolysis results in the formation of anthraquinone(II b).

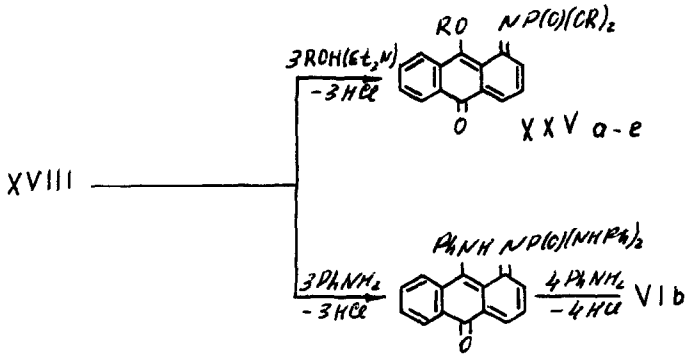


In certain cases splitting of halogen hydride out of aminoanthraquinone derivatives (XIX,XXI) is a predominant process,i.e. the formed anthrones (XIX,XXI,XXIII) are immediately transformed into anaquinoneimines (XX,XXII, XXIV).



The hydrolysis of anaquinoneimines (XVIII,XX,XXII,XXIV) proceeds at room temperature and results in the decomposition of molecules to anthraquinone (II b).

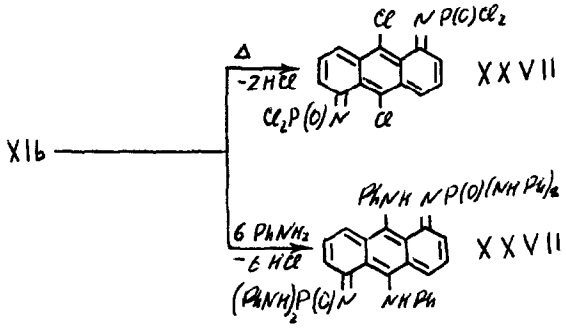
Unlike the reactions of anaquinoneimine (XVII),which do not produce individual products,alcoholysis and aminolysis of anaquinoneimine (XVIII) proceed resulting in the substitution of chlorine atoms and formation of the corresponding alkoxy- and amino-derivatives of anaquinoneimine (XXV a-e,XXVI).



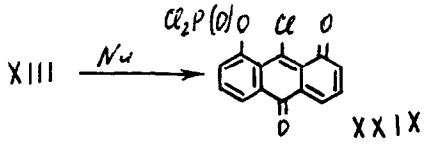
R=Me(a), Et(b), Pr(c), i-Pr(d), iBu(e)

Anaquinoneimine (XXVI) is also formed upon the interaction of anthrone(VI b) and aniline.

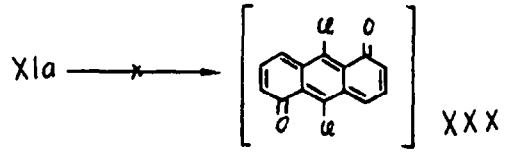
In general, chemical behaviour of 1,5- and 1,8-disubstituted derivatives of anthraquinone (XI a,b, XIII) is similar to that of monosubstituted anthrones (VI a-c) which can be exemplified by thermolysis and aminolysis of tetrahydroanthracene (XI b) producing the corresponding anaquinonediimines (XXVII, XXVIII).



or by the transformation of anthrone (XIII) into anaquinone (XXIX) upon the reaction with nucleophiles.

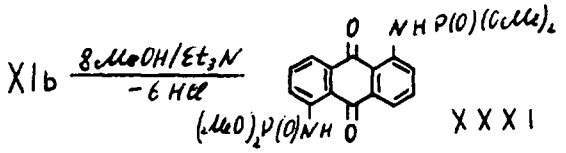


In certain reactions the peculiar character of disubstituted compounds is revealed. In particular, dehydrochlorination of tetrahydroanthracene (XI a) with the formation of 1,5-anthraquinone (XXX) is not observed and this is probably due to the extreme instability of the former.



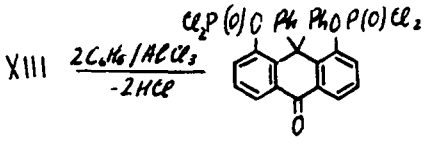
XXX

The interaction of tetrahydroanthracene (XI b) with methanol proceeds in a different way, compared to the reaction of anthrone (VI b) and alcohols, and causes the formation of anthraquinone (XXXI).



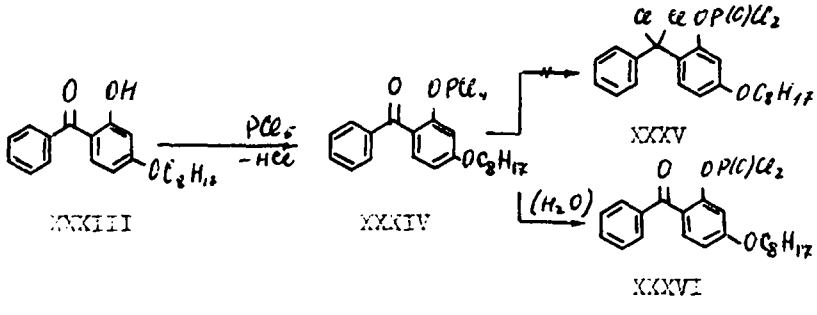
XXXI

In case of anthrone (XIII), the electrophilic substitution reaction with the participation of benzene is possible which results in the formation of bisphosphorylated diphenylsubstituted anthrone (XXXII).



XXXII

During the interaction of PCl_5 with 2-oxybenzophenon (XXXIII), the opening of a ketone carbonyl group was expected as in case of 1-oxy-9,10-anthraquinone, and the formation of a product having geminal chlorine atoms (XXXV). However, the reaction stops during the formation of benzophenone (XXXIV) released from the reaction mixture in the form of benzophenone (XXXVI).



XXXIII XXXIV XXXV XXXVI

Thus, the discovered reaction of anthraquinone cyclization is not realized in case of 2-oxy-benzophenones and this phenomenon can obviously be explained by the specific character of electron influence transfer from substituents to a carbonyl group contained in anthraquinones.

Experimental

Crystal Structure Determination.

Crystal data: $C_{14}H_8Cl_8N_2O_2P_2 \cdot M = 578$, monoclinic, space group P $2_1/C$, a = 13.305(7), b = 12.685(5), c = 9.692(5) Å, β = 110.36(4)°, D_x = 1.71 g/cm^{-3}, Z = 4.

Data collection. Intensity data collection and cell determination were performed at 20°C using a four-circle automated Enraf-Nomius CAD-4 diffractometer with graphite monochromized Mo-K radiation. 2304 independent reflections with $F^2 \geq 3\sigma$ were gathered within the limit $\theta \leq 30°$ with $\omega/(5/3\,\theta)$ scanning mode.

Structure analysis. The structure was solved by direct methods using MULTAN program and refined in anisotropic approximation. All hydrogen atoms were located in a difference Fourier synthesis and refined isotropically in the final cycles of full-matrix least-squares.

At the final stages 2006 reflections with $F^2 \geq 7\sigma$ yielded conventional R = 0.038 and R_w = 0.050

Spectroscopic Data.

Mass-spectra were obtained with a MAT-212 spectrometer (Finigan) with a direct inlet system at 50 eV and 0.1 mA. ^1H and ^{31}P NMR spectra were recorded in acetone and acetonitrile solutions using Bruker spectrometers (80 and 250 MHz).

IR spectra were measured on a UR-20 spectrometer in CCl_4, $CHCl_3$ solutions and in nujol. Commercial solvents and reagents were used.

Physico-chemical characteristics, IR, NMR and mass-spectra data of the compounds are given in Tables 2-4.

Mehtod A.

0.02 Mol of anthraquinone (II a) or (II b) and 0.02 Mol of phosphorane (I a), or (I b), or (I c), or (I d), or (I e) were refluxed in 50 ml of benzene until HCl or HBr stops to evolve.

Method B.

0.03 Mol of 1,5-dioxy-9,10-anthraquinone or 1,5-diamino-9,10-anthraquinone and 0.06 mol of PCl_5 were refluxed in 100 ml of benzene until HCl stops to evolve. The precipitate obtained was filtered off and washed with hot benzene. The residue was recrystallized.

Method C.

0.02 Mol of 1,8-dioxy-9,10-anthraquinone or 1,4-dioxy-9,10-anthraquinone or 1,4-diamino-9,10-anthraquinone and 0.04 mol of PCl_5 were refluxed in 100 ml of benzene until HCl stops to evolve.Benzene was removed under vacuum.The residue was recrystallized.

Method D.

To a solution containing 0.02 mol of anthraquinone (VI a) or (VI b) in 100 ml of benzene,a solution of 0.03 mol of methyl or ethyl alcohol or dibutyl ether or triethylamine or dimethylaniline or butylmercaptan in 20 ml of benzene was added at room temperature.The mixture was refluxed until the completion of the formation of amine hydrochloride precipitate or until HCl stops to evolve.The precipitate was filtered off and washed by benzene. The filtrate was evaporated under vacuum.The residue was recrystallized.

Method E.

The solution of 0.015 mol of anthrone (VI b) in 20 ml of o-xylene was refluxed until HCl stops to evolve.The solvent was removed under vacuum. The residue was recrystallized.

Method F.

Gaseous HCl was passed through the solution of 0.05 mol of anthraquinone (XVIII) in 50 ml of benzene for 1.5 hours at room temperature.The solvent was removed under vacuum.The residue was recrystallized.

Method G.

To a solution containing 0.02 mol of anaquinoneimine (XVIII) and 0.06 mol of alcohol (ROH) in 80 ml of benzene,a solution of 0.03 mol of triethylamine in 10 ml of benzene was added at room temperature for two hours. Triethylamine hydrochloride precipitate was filtered off.The filtrate obtained was evaporated under vacuum.The residue was recrystallized.

Method H.

To a solution containing 0.02 mol of anthraquinoneimine (XVIII) in 100 ml of benzene,a solution of 0.12 mol of aniline in 50 ml of benzene was added at temperature 0 + 5°C.The reaction mixture was stirred at this temperature for 1 hour and refluxed for 1.5 hours.From the hot reaction mixture a precipitate was filtered off which was washed with hot water to remove aniline hydrochloride .The residue was dried under vacuum at 50°C and then recrystallized.

Method I.

To a solution containing 0.02 mol of anthrone (VI b) in 100 ml of benzene,a solution of 0.14 mol of aniline in 70 ml of benzene was added at room temperature 0 + 5°C. The reaction mixture was stirred at this temperature for 2.5 hours.Then the procedures given in Method H were repeated.

Method J.

A solution of 0.02 mol of tetrahydroanthracene (XI b) in 70 ml of o-xylene was refluxed until HCl stops to evolve for 1 hour.From the hot reaction mixture a precipitate was filtered off.70 ml of heptane was added to a cooled filtrate.The precipitate obtained was filtered and recrystallized.

Method K.

A solution of a reaction mixture containing 0.04 mol of tetrahydroanthracene (XI b) and 0.56 mol of aniline in 170 ml of benzene was prepared.Then the procedures given in Method I were repeated.

Method L.

A solution of a mixture containing 0.02 mol of anthrone (XIII) and 0.02 mol of triethylamine or dibutyl ether in 100 ml of benzene was refluxed for 2 hours.The precipitate was filtered off.Benzene,triethylamine or dibutyl ether and phosphorus oxychloride were distilled off the filtrate under vacuum.The residue was recrystallized.

Method M.

A solution of a reaction mixture containing 0.02 mol of tetrahydroanthracene (XI b),0.16 mol of methanol and 0.12 mol of triethylamine in 100 ml of benzene was prepared.All the procedures given in Method G were repeated.

Method N.

A suspension of a mixture containing 0.04 mol of anthrone (XIII) and 0.12 mol of aluminium trichloride in 150 ml of benzene was refluxed until HCl stops to evolve (for 1.5 hours).From the reaction mixture a precipitate was filtered off.The filtrate was evaporated under vacuum.The residue was recrystallized.

Method O.

A solution of the mixture containing 0.01 mol of 2-oxy-benzophenone (XXXIII) and 0.01 mol of PCl_5 in 100 ml of benzene was refluxed until HCl

stops to evolve. The precipitate was filtered off. The filtrate was evaporated under vacuum. The residue was deposited by pentane from acetone.

Hydrolysis of Anthrone (VIa).

To a solution containing 0.015 mol of anthrone (VIa) in 20 ml of acetone, 200 ml of water was added while stirring. The reaction mixture was stirred for 30 minutes at room temperature. Anthraquinone (IIa) obtained was filtered off. The yield is 100%.

The hydrolysis of anthrone (VIb) was performed in a similar way. The yield of anthraquinone (IIb) is 100%.

The hydrolysis of anaquinoneimines (XVIII,XX,XXII,XXIV) was performed in a similar way.

The yield of anthraquinone (IIb) is 100%.

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