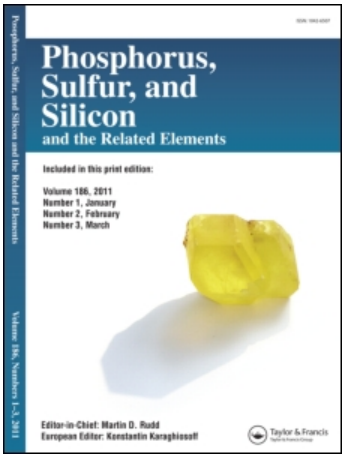

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INVESTIGATION IN THE CHROMONE SERIES. PART XIX. REACTION OF THE CHLORIDES OF CHROMONE-2- AND -3-CARBOXYLIC ACID WITH PHOSPHITES. PERKOW REACTION IN THE PRESENCE OF CONJUGATE DOUBLE BONDS

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INVESTIGATION IN THE CHROMONE SERIES. PART XIX.† REACTION OF THE CHLORIDES OF CHROMONE-2- AND -3-CARBOXYLIC ACID WITH PHOSPHITES. PERKOW REACTION IN THE PRESENCE OF CONJUGATE DOUBLE BONDS.

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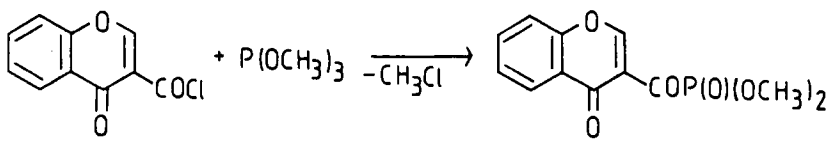
4-Oxo-4H-1-benzopyran-3-carbonyl chloride forms in a Michaelis-Arbuzov reaction the corresponding α-ketophosphonate. As a result of further Michaelis-Arbuzov and Perkow reactions with tertiary phophites 4-oxo-4H-1-benzopyran-2-carbonyl chloride forms two stereoisomeric products (E) and (Z). The mechanism of their formation and the structure has been suggested on the basis of spectroscopic dates and reactions with proton nucleophilic reagents.

Key words: Dimethyl (4-oxo-4H-1-benzopyran-3-yl)carbonylphosphonate, (E) and (Z) 2(dialkylphosphato, dialkylphosphono)methylene - 4[(4 - oxo - 4H - 1 - benzopyran - 2 - yl)carbonyloxy]2H - 1 - benzopyran; synthesis, structure, reaction mechanism.

Chromone (4-oxo-4H-1-benzopyran) compounds are known for their biological activity (flavonoids, furanochromones). Hitherto, the phosphoric derivatives of this group have not been described. Only chromone-2-methanephosphonic acid and its diethyl ester[1] has been obtained. In our previous investigations we obtained a number of chromone-2- and -3-hydroxymethane and methanephosphonic acids and esters.[2]

The aim of this study is the synthesis of α-ketophosphonic esters and acids of chromone, which we planned to prepare in the reactions of chromone-2- and chromone-3-carbonyl chlorides with tertiary phosphites.

The acid chlorides react with trialkyl phosphites either to the corresponding α-ketophosphonic esters (Michaelis-Arbuzov reaction)[3] or to phosphoric[4–6] or vinyl phosphoric derivatives (Perkow reaction).[7] In the reaction of 4-oxo-4H-1-benzopyran-3-carbonyl chloride **1** with trimethylphosphite **4a** we obtained the expected dimethyl (4-oxo-4H-1-benzopyran-3-yl) carbonylphosphonate **2** (Scheme I).



1 2

SCHEME I

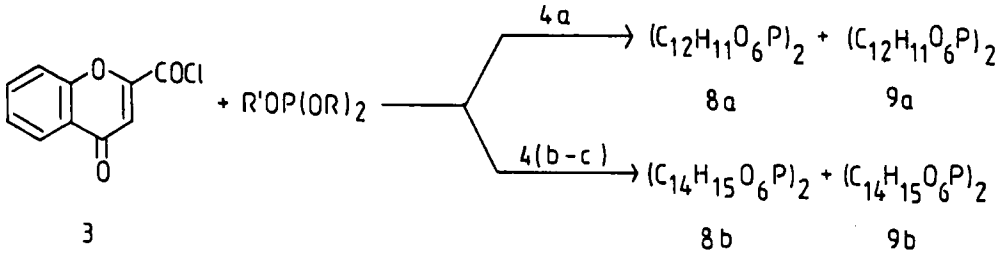
†Part XVIII, see Reference 2.

Compound **2** is a colourless, crystalline solid easily soluble in aprotic solvents. In the presence of proton donor solvents **2** is unstable, because the labile[3] C(O)—P bond is cleaved. The appreciable unstability of compound **2** is confirmed by MS spectroscopy (the parent ion M^+ 282 is not observed).

In the reaction of 4-oxo-4H-1-benzopyran-2-carbonyl chloride **3** with trimethylphosphite **4a** or triethylphosphite **4b** and diethyltrimethylsilylphosphite **4c** two series of isomeric compounds **8a** and **8b**, **9a** and **9b** were obtained instead of the respective α-ketophosphonate esters. Their molecular formulas $(C_{12}H_{11}O_6P)_2$ and $(C_{14}H_{15}O_6P)_2$ indicate the dimeric structure of α-ketophosphonic esters (see Scheme II).

Compounds **8** and **9** are coloured, crystalline solids easily soluble in aprotic solvents, and very unstable in protic solvents. Compounds **8** show more intense colour (orange) than **9**. They are formed with good total yields, independent of reaction conditions (e.g., temperature, change of order of reagent addition). ^{31}P NMR analysis carried out during the reaction indicated the effect of temperature on the ratio of the formed isomers **8(a–b)** to **9(a–b)**: at −40°C it was 3:1, and at +60°C 6:1 respectively. It suggests that the formation of the structures **8** was kinetically favoured. Apart from the ^{31}P chemical shift values characteristic for the dimers of **8** and **9** no other ^{31}P chemical shifts were observed which would indicate e.g. the formation of an intermediate α-ketophosphonic compound of the structures C(O)—P. The thermal isomerization of less stable isomers **8(a–b)** to thermodynamically more stable **9(a–b)** was observed.

The compounds **8** and **9** have similar ^{31}P chemical shifts and identical coupling constants J_{PP}. The observed shifts of the phosphorus nuclei are characteristic of C—P[2,6,7] and C—O—P[6,7] groups. In the ^1H NMR spectra the compounds **8** and **9** show only characteristic signals for protons of the alkyl groups and protons of the aromatic system. The signal of the proton at C_3 was observed at a higher field (~6.5 ppm) in compounds **10** than in the isomers **8** and **9** (~6.7–8.2 ppm). IR spectra of **8** and **9** are identical except the absorption bands in the ranges 1390–1370 and 1250–1205 cm^{-1}. Compounds **8** show a wide intensive absorption band,



4a: R' = R = CH_3-
4b: R' = R = C_2H_5-
4c: R' = $(CH_3)_3Si$-; R = C_2H_5-

SCHEME II

while compounds **9** give two medium absorption bands at 1390 and 1370 and three bands at 1250, 1225, 1205 cm^{-1} (see Table).

Interesting informations were obtained from the chemical properties of the isomeric compounds **8** and **9**. Both **8** and **9** react easily with protic reagents: water, methanol, primary and secondary amines forming, with quantitative yield, compounds **10(a–b)** and, depending on the applied reagent, either chromone-2-carboxylic acid or its derivatives: ester or amide **12**. On the basis of microanalysis and spectroscopic studies compounds **10** have been identified as 2(dialkylphosphato, dialkylphosphono)methyl-4H-1-benzopyran-4-one. The course of reaction is as follows (Scheme III).

The investigated reaction (Scheme III) of compounds **8** and **9** with protic reagents, as well as micro- and spectral analysis of this compounds show that they are (E) and (Z) stereoisomers of 2(dialkylphosphato, dialkylphosphono)methylene-4[(4-oxo-4H-1-benzopyran-2-yl)carbonyloxy]2H-1-benzopyran.

DISCUSSION OF THE REACTION MECHANISM

On the basis of the so far investigated reactions of acid chlorides with trialkyl phosphites, as well as chemical and physical properties of products and reactants the following course of changes can be presented (Scheme IV).

At the first step, compound **3** reacts with **4(a–c)** and forms unstable dialkyl α-ketophosphonate **5** (Michaelis-Arbuzov product). The second molecule of phosphite may attack either the carbon atom[4] or the oxygen atom[6,7] of compound **5**. The binding of the phosphorus to the oxygen atom is more probable because of the presence of two strongly electron withdrawing substituents at the acyclic carbon atom causing reversal of the polarization of the carbonyl group. The formed unstable compound **6** is stabilized by displacement of the charge through the conjugated system of π bonds to the thermodynamically more stable betain structures **7**, with the formation of a double bond between carbon C_2 and the acyclic carbon (Perkow reaction). As a result of the electrophilic attack of compound **3** on the oxoanionic form of compounds **7**, two stereoisomers **8** and **9** are formed. The formation of the ester bond with simultaneous (or later) dealkylation of the $\overset{+}{O}P(OCH_3)_3$ group by the Cl^- anion stabilizes both compounds **8** and **9**. The confirmation of the assumed course of the reaction comes from the reaction of compound **3** with **4a** in the presence of proton donor compounds HX, as well as from the reaction with diethyltrimethylsilylphosphite **4c**. In the reaction of compound **3** with **4a** in the presence of HX, the formed carboanionic structure **6** was protonated to the stable compound **10a**. The group $\overset{+}{O}P(OCH_3)_3$ is dealkylated by the X^- anion forming methyl benzoate or methyl chromone-2-carboxylate ester.

In the investigated reaction of compound **3** with **4c** stereoisomers **8b** and **9b** were obtained. They could be formed by the suggested path. In the case of initial attack of compound **4c** on the carbonyl carbon of compound **5** and subsequent migration of the electrophilic trimethylsilyl group[8] to the oxygen atom at the α-position, 2[bis(diethylphosphono)trimethylsilyloxy]methyl-4H-1-benzopyran-4-one should be formed, and after hydrolysis—its α-hydroxydiphosphonic derivative; but such a change was not observed. Thus initial attack on the carbonyl carbon atom can be ruled out.

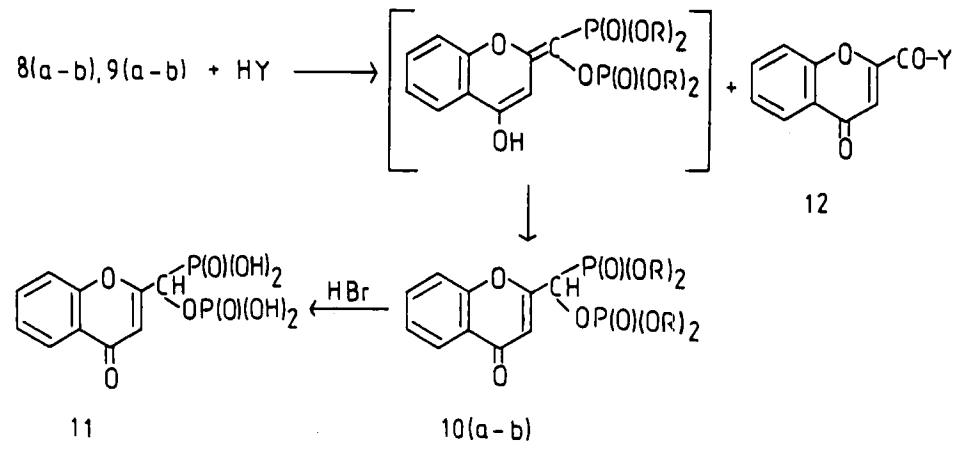
TABLE

Summary formula, molecular mass, analyses and spectral data of compounds **2** to **11**

Compound No.	Summary formula Molecular mass	Analyses % Calcd./Found C	H	P	^{31}P NMR	IR	^{1}H NMR	MS, m/z (%)
2	$C_{12}H_{11}O_6P$ (282,18)	51,07 51,10	3,93 4,10	10,98 10,63	−0,73	1655(—CO—P) 1620(C=O) 1250(P=O) 1035(P—O—C)	3,89(d, 6H, $2CH_3$, J_{PH} = 11 Hz); 7,3–8,3 (m, $4H_{arom.}$); 8,9(d, 1H, C_2H, J_{PH} = 0.5 Hz)*	204(M^+ −78,13), 173(42), 161(20), 147(9), 146(100), 121(29), 120(13), 104(18), 92(10), 80(23), 79(25), 66(39), 65(25), 63(14), 47(23), 30(14), 17(17), 14(13).
8a	$C_{24}H_{22}O_{12}P_2$ (564,37)	51,07 50,91	3,93 4,01	10,98 10,91	12,74; 0,42 J_{PP} = 4,31 ± 1,45 Hz	1758(—C/O/—O) 1660(C=O) 1390 1220(P=O) 1065(P—O—C)	3,73; 3,83(2d, 12H, $4CH_3$, $^3J_{PH}$ = 11 Hz); 6,8–8,2(m, 10H, $8H_{arom.}$, C_3H, C_3H)	392(M^+ −172,5), 298(9), 204(43), 176(26), 174(9), 173(9), 149(12), 146(13), 145(54), 120(20), 118(12), 110(12), 109(59), 104(13), 102(16), 101(11), 95(12), 93(34), 92(56), 89(100), 79(24), 76(37), 74(29), 69(30), 64(24), 63(75), 62(24), 59(24), 53(36), 50(46).
8b	$C_{28}H_{30}O_{12}P_2$ (620,47)	54,20 54,10	4,87 5,10	9,98 9,80	10,14; −1,40 J_{PP} = 4,52 ± 1,80 Hz	1758(—C/O/—O) 1658(C=O) 1390 1225(P=O) 1065(P—O—C)	1,30(t, 12H, $4CH_3$); 4,16; 4,22(dq, 8H, $4CH_2$); 6,9–8,25(m, 10H, $8H_{arom.}$, C_3H, C_3H)	
9a	$C_{24}H_{22}O_{12}P_2$ (564,37)	51,07 50,70	3,93 3,95	10,98 10,72	14,23; −1,32 J_{PP} = 7,48 ± 1,45 Hz	1762(—C/O/—O) 1650(C=O) 1390, 1370 1250 1225(P=O) 1205 1050(P—O—C)	3,68; 3,84(2d, 12H, $4CH_3$, J_{PH} = 10 Hz); 6,9–8,2(m, 10H, $8H_{arom.}$, C_3H, C_3H)*	564(M^+, 34), 392(10), 217(16), 173(21), 145(19), 109(42), 93(100), 92(10), 89(52), 79(10), 63(10), 15(11).

9b	$C_{28}H_{30}O_{12}P_2$ (620,47)	54,20 54,02	4,87 4,98	9,98 10,10	11,29; −3,88 J_{PP} = 7,40 ± 1,80 Hz	1750(—C/O/—O) 1658(C═O) 1390, 1370 1250 1225(P═O) 1205 1050(P—O—C)	1,28; 1,35(2t, 12H, $4CH_3$) 4,15; 4,20(dq, 8H, $4CH_2$); 6,97–8,23(m, 10H, $8H_{arom.}$, C_3H, C_3H)	483(M^+ − 137,6), 468(18), 448(12), 447(10), 333(13), 332(65), 331(12), 330(10), 318(11), 311(13), 304(13), 296(11), 295(11), 255(16), 191(27), 175(14), 174(12), 173(52), 160(18), 147(11), 146(33), 145(44), 127(11), 121(67), 120(12), 109(25), 107(15), 101(20), 99(17), 93(24), 92(16), 91(12), 89(100), 81(38), 65(23), 29(32), 28(36), 27(12), 18(19).
10a	$C_{14}H_{18}O_9P_2$ (392,21)	42,87 43,03	4,62 4,77	15,79 16,00	16,58; 1,90 J_{PP} = 31,98 ± 1,45 Hz	1620(C═O) 1262(P═O) 1050(P—O—C)	3,68; 3,72; 3,98(3d, 12H, $4CH_3$, $^3J_{PH}$ = 10 Hz); 5,74; 5,94(dd, 1H, CH, J_{PH} = 11 Hz, J_{PH} = 14 Hz), 6,5(d, 1H, C_3H, $^4J_{PH}$ = 2 Hz); 7,26–8,11(m, $4H_{arom.}$)	392(M^+, 39), 360(9), 283(37), 268(17), 266(17), 219(10), 203(7), 187(12), 173(11), 131(9), 120(9), 109(100), 93(49), 92(16), 79(18), 63(10).
10b	$C_{18}H_{26}O_9P_2$ (448,31)	48,22 48,05	5,84 5,61	13,84 14,05	13,84; 0,29 J_{PP} = 28,11 ± 1,80 Hz	1650(C═O) 1265(P═O) 1050(P—O—C)	1,25(t, 6H, $2CH_3$); 4,11; 4,16(dq, 4H, $2CH_2$); 5,62 5,78(dd, 1H, CH, J_{PH} = 11 Hz, J_{PH} = 14 Hz); 6,57(d, 1H, C_3H, $^4J_{PH}$ = 2 Hz); 7,22–8,20(m, $4H_{arom.}$)	448(M^+, 10), 296(7), 219(100), 218(13), 190(42), 173(14), 162(27), 160(10), 146(20), 145(11), 120(14), 118(8), 105(17), 99(14), 92(20), 89(54), 81(14), 76(14), 57(15), 50(12), 43(16), 39(12), 29(62), 28(16), 27(25), 18(32).
11	$C_{10}H_{10}O_9P_2$ (336,13)	35,73 35,50	3,00 2,90	18,43 18,15	10,59; 0,32 J_{PP} = 29,33 ± 2,91 Hz**	3200 − −2400(POH) 1610(C═O) 1230(P═O) 1035(P—O—C)	4,96; 5,11(dd, 1H, CH, J_{PH} = 11 Hz, J_{PH} = 15 Hz); 6,31(d, 1H, C_3H, $^4J_{PH}$ = 2 Hz); 7,20–8,15(m, $4H_{arom.}$); 10,20(s, 4H, 2 P/OH/$_2$)	

*in $CDCl_3$.
**in D_2O.



a: R = CH_3-, b: R = C_2H_5- Y = -OH, $-OCH_3$, $-HNC_3H_7$, $-N(C_3H_7)_2$, $-N(C_4H_9)_2$, $-HNC_6H_5$

SCHEME III

EXPERIMENTAL

Melting points are uncorrected. IR spectra were taken on a Pye-Unicam 200G spectrometer, in KBr (tablets), ν. ^1H NMR spectra were recorded at 60 MHz using a Varian EM-360 spectrometer, in DMSO-d_6, and ^{31}P NMR spectra on a Bruker HX 360 spectrometer, in C_6D_6. Mass spectra were measured on LKB-2091 and Varian MAT 711 spectrometers (at 70 eV ionizing energy). All solvents were dried according to standard methods (benzene and toluene were distilled over $LiAlH_4$). Argon was dried with concentrated H_2SO_4 and P_2O_5.

Dimethyl (4-oxo-4H-1-benzopyran-3-yl)carbonylphosphonate (**2**). 4-Oxo-4H-1-benzopyran-3-carbonyl chloride,[9] **1**, 4.17 g (0.02 mol), was dissolved in 10 ccm of anhydrous benzene. At +5°C in a dry argon atmosphere 2.48 g (0.02 mol) of freshly distilled trimethyl phosphite **4a** was added dropwise. Then the reaction mixture was stirred for 4 h at that temperature, and then for 1.5 h at room temperature. A colourless precipitate was filtered off and from the filtrate benzene was evaporated under reduced pressure. The oily residue solidified on cooling. The combined precipitates were crystallized from anhydrous THF. 3.67 g (65%), mp. 100–102°C of compound **2** were obtained.

(E) and (Z) 2(dimethylphosphato, dimethylphosphono)methylene-4[(4-oxo-4H-1-benzopyran-2-yl)carbonyloxy]2H-1-benzopyran (**8a**) *and* (**9a**).

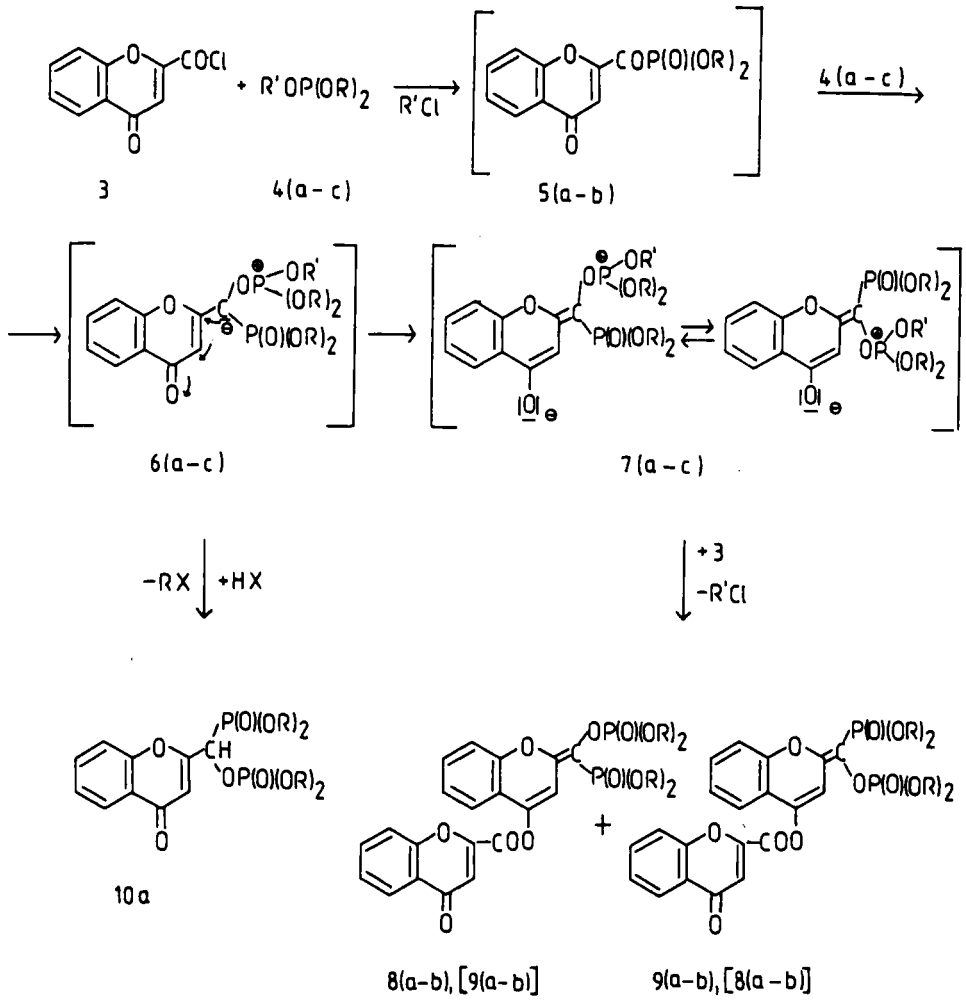
a. Reaction of **3** *with* **4a** *at −40°C.* 4.17 g (0.02 mol) of 4-oxo-4H-1-benzopyran-2-carbonyl chloride[10] **3** was added to 25 ccm of anhydrous toluene, cooled to −40°C. Then, under dry argon, 2.48 g (0.02 mol) of freshly distilled **4a** was added dropwise. The mixture was stirred for 3 h, and then at room temperature for 2 h. The yellow precipitate was filtered off. From the filtrate toluene was distilled off under reduced pressure and the residue cooled. 4.9 g (87%), mp. 140–156°C of the mixture of products **8a** and **9a** were obtained.

The compounds were separated by column chromatography (silica gel 60, 70–230 mesh ASTM, Merck; anhydrous acetone).

Obtained: **8a**, 3.2 g (56.7%), pm. 153–157°C (acetone), orange needles, R_f = 0.30 (silica gel, acetone).
9a, 1.12 g (20%), mp. 176–178°C (acetone), light yellow needles, R_f = 0.65 (silica gel, acetone).

The mixture of **8a** and **9a** can also be separated by fractional crystallization from anhydrous acetone.

b. Reaction of **3** *with* **4a** *at +60°C.* The reaction was carried out as described in a, with the following modification: (i) reaction temperature +60°C; (ii) when all **4a** had been added the temperature was



SCHEME IV

kept at +60°C for 15 minutes; (iii) after distilling off toluene under reduced pressure several ccm of cold anhydrous diethyl ether were added to the oily residue. The yellow precipitate of compounds **8a** and **9a** was filtered off.

Obtained: 4.5 g (80%), mp. 138–150°C of **8a** and **9a**. Separated as described in a.
Obtained: **8a**, 3.05 g (54%), mp. 153–157°C (acetone), **9a** 0.72 g (12.8%), mp. 177–179°C (acetone).

(E) and (Z) 2(diethylphosphato, diethylphosphono)methylene-4[(4-oxo-4H-1-benzopyran-2-yl)carbonyloxy]-2H-1-benzopyran (**8b**) *and* (**9b**).

a. Reaction of **3** *with* **4b** *at −40°C.* 4.17 g (0.02 mol) of compound **3** in 25 ccm of anhydrous toluene were cooled to −40°C and 3.32 g (0.02 mol) of freshly distilled **4b** was added in a dry argon atmosphere with vigorous stirring. After adding phosphite the mixture was stirred for 2 h at −40°C, and then for 4 h at room temperature. Toluene was distilled off under reduced pressure. The yellow oily residue solidified on cooling. After washing with several ccm of cold anhydrous diethyl ether, 4.53 g (73%) of a light yellow precipitate of the mixture of products **8b** and **9b** were obtained (mp. 97–115°C). They were separated by column chromatography (silica gel 60, 70–230 mesh ASTM, Merck; anhydrous acetone:ethyl acetate 1:1).

Obtained: **8b**, 2.60 g (41.9%), mp. 105–108°C (benzene), orange-yellow prisms, R_f = 0.32 (silica gel, acetone:ethyl acetate 1:1), **9b**, 1.07 g (17.2%), mp. 152–154°C (benzene), light yellow prisms, R_f = 0.55 (silica gel, acetone:ethyl acetate 1:1).

b. Reaction of **3** *with* **4b** *at +60°C.* Reaction was carried out as described in a. 3.85 g (62%) of a yellow precipitate with mp. 95–116°C of the mixture of **8b** and **9b** were obtained. They were separated as described in a.

Obtained: **8b**, 2.46 g (42.5%), mp. 105–108°C (benzene), **9b**, 0.51 g (8.3%), mp. 153–155°C (benzene).

c. Reaction of **3** *with* **4c**. 4.17 g (0.02 mol) of compound **3** were dissolved in 25 ccm of anhydrous benzene. 4.21 g (0.02 mol) of compound **4c** were added dropwise in a dry argon atmosphere, at +10°C with stirring. The temperature was kept for 6 h. Benzene was distilled off under reduced pressure. The residue, a yellow oil, was washed with several ccm of anhydrous diethyl ether and cooled. There was obtained 4.3 g (69.3%) of a yellow precipitate of the mixture of **8b** and **9b**, mp. 96–116°C. They were separated by means of column chromatography (as described in a).

Obtained: **8b**, 1.65 g (26.6%), mp. 105–106°C (benzene), **9b**, 2.05 g (33%), mp. 153–155°C (benzene).

Thermal conversion of **8a** *into* **9a**. 1.13 g (0.002 mol) of compound **8a** were refluxed in 25 ccm of benzene (argon atmosphere) for 24 h. The solution gradually changed the colour from orange to yellow (TLC control). Benzene was distilled off under reduced pressure. The light yellow oil solidified on cooling.

Obtained: 0.65 g (57.5%), mp. 177–179°C (acetone) of compound **9a**.

Thermal conversion of **8b** *into* **9b**. 1.24 g (0.002 mol) of compound **8b** were heated for 50 h as described for compound **8a**.

Obtained: 0.60 g (48%), mp. 154–156°C (benzene) of compound **9b**.

2(dimethylphosphato, dimethylphosphono)methyl-4H-1-benzopyran-4-one (**10a**).

Reaction of **3** *with* **4a** *in the presence of proton donor HX compounds.*

a. Reaction in the presence of benzoic acid. 2.08 g (0.01 mol) of compound **3** and 1.22 g (0.01 mol) of benzoic acid were added to 30 ccm of anhydrous benzene. 2.48 g (0.02 mol) of freshly distilled **4a** was added dropwise at +10°C (argon atmosphere) with stirring. After adding **4a** the reaction mixture was stirred for 2 h at room temperature. Benzene was distilled off under reduced pressure. The oily residue was purified by column chromatography (silica gel 60, 70–230 mesh ASTM, Merck; acetone).

Obtained: **10a**, 3.05 g (77.8%), mp. 106–108°C (THF), colourless prisms, R_f = 0.40 (silica gel, acetone) and 1.17 g (86%) of methyl benzoate.

b. Reaction of **3** *with* **4a** *in the presence of 4-oxo-4H-1-benzopyran-2-carboxylic acid.* 2.08 g (0.01 mol) of compound **3** and 1.9 g (0.01 mol) of 4-oxo-4H-1-benzopyran-2-carboxylic acid were added to 300 ccm of anhydrous dioxane. 2.48 g (0.02 mol) of freshly distilled **4a** was added dropwise at room temperature in a dry argon atmosphere, with sitrring for 6 h. Dioxane was distilled off under reduced pressure. The oily residue was purified by column chromatography (conditions as described in a).

Obtained: **10a**, 2.86 g (76%), mp. 106–108°C (THF) and methyl 4-oxo-4H-1-benzopyran-2-carboxylate 1.16 g (57%), mp. 122–124°C (methanol), (Literature 11 mp. 121–123°C).

Reaction of compounds **8(a–b)** *or* **9(a–b)** *with nucleophilic reagents HY.*

a. Reaction with water. 0.002 mol of compound **8(a–b)** or **9(a–b)** were heated with 15 ccm of water for 30 minutes. The yellow precipitate slowly dissolves and loses colour. After cooling, colourless crystals of 4-oxo-4H-1-benzopyran-2-carboxylic acid (85–90%) mp. 254°C (decomp.) (methanol), (Literature 11 mp. 260°C) (decomp.) were obtained. After distilling off the water under reduced pressure the oily residue solidified on cooling.

Obtained: **10a**, (80–90%), mp. 105–107°C (THF), **10b**, (80%), mp. 61–63°C (diethyl ether), colourless prisms, R_f = 0.38 (silica gel, acetone:ethyl acetate 1:1).

b. Reaction with methanol. 0.002 mol of compound **8(a–b)** or **9(a–b)** were refluxed with 10 ccm of anhydrous methanol for 1 h. The yellow solution slowly loses colour. From the oily residue, after evaporating methanol to 5 ccm under reduced pressure and then placing in a refrigerator, methyl 4-oxo-4H-1-benzopyran-2-carboxylate (85–90%) was obtained. From the filtrate, after evaporating methanol, the compounds **10a** (80–90%) or **10b** (70–80%) were obtained.

c. Reaction with amines. To 0.002 mol of compound **8(a–b)** or **9(a–b)** in 20 ccm of anhydrous benzene, 0.002 mol of an appropriate amine HY diluted with 5 ccm of anhydrous benzene were added dropwise at room temperature, with stirring. The yellow precipitate slowly dissolves and loses colour. Then the solution was concentrated to 10 ccm and cooled. A precipitate of the appropriate amide **12** was obtained:

propyl-4-oxo-4H-1-benzopyran-2-carboxamide 0.39 g (85%), mp. 175–177°C (xylene), (Literature 12 mp. 174–175°C).

dipropyl-4-oxo-4H-1-benzopyran-2-carboxamide 0.44 g (81%), mp. 182–183°C (xylene), Literature 12 mp. 182–183°C).

dibutyl-4-oxo-4H-1-benzopyran-2-carboxamide 0.5 g (83%), mp. 156–158°C (benzene), (Literature 12 mp. 158–159°C).

phenyl-4-oxo-4H-1-benzopyran-2-carboxamide 0.47 g (89%), mp. 225–227°C (ethanol, water), (Literature 13 mp. 223–225°C).

From the filtrate which was evaporated and cooled **10a** (85–90%) or **10b** (75–80%) were obtained.

2(Dihydroxyphosphato, dihydroxyphosphono)methyl-4H-1-benzopyran-4-one (**11**). 3.92 g (0.01 mol) of compound **10a** were dissolved in 5 ccm of glacial acetic acid, and a stoichiometric amount of 40% HBr solution in acetic acid was added. The reaction mixture was left at room temperature for 24 h. Acetic acid was distilled off. The oily residue was dissolved in 10 ccm of anhydrous ethanol, and cooled after adding 20 ccm of anhydrous acetone.

Obtained: **11**, 1.88 g (56%), mp. 215°C (decomp.).

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