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Triphenylphosphanodefluorination of fluoranil and its derivatives

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ABSTRACT

The reaction of 2-X-trifluoro-1,4-benzoquinones (X = F, Cl, Me, OMe) with triphenylphosphane in various solvents (C_6H_6, Et_2O, THF, dioxane, MeOH, aq. dioxane and Me_2SO) has been investigated. It was shown that: (1) the quinones react with PPh_3 at an oxygen atom and at a carbon atom with formation of products of reduction and of triphenylphosphanodefluorination, accordingly; (2) the use of more polar solvents, such as MeOH, aq. dioxane and Me_2SO, leads to an increase in products of phosphanodefluorination; (3) triphenylphosphanodefluorination of 2-X-trifluoro-1,4-benzoquinones (X = Cl, Me, OMe) takes place at positions 5 and 6 to X in ratios depending on the nature of the substituent X. Possible reasons for obtained results are discussed in detail. The entry of solvent molecule into products of phosphanodefluorination of fluoranil was observed in MeOH. The triphenyl(3,4,6,6-tetrafluoro-2-oxido-5-oxocyclohexa-1,3-dien-1-yl)phosphanium and its analogs serves as starting material for a new type of nitrogen-containing phosphorus compounds. The structures of isolated betaines were proved by the XRD and the ^{19}F, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data.

1. Introduction

Many found in nature [1] and synthesized 1,4-benzoquinone derivatives exhibit high and various biological activity [2a–d]. 1,4-Naphthoquinone derivatives showed antioxidant and anti-malarial properties [3a,b]. Polyfluorinated functionalized 1,4-naphthoquinones can be inhibitors of cancer cells growth [4a–f]. As recently reported reactions hexa- and 2,5,6,7,8-pentafluorophenyl 1,4-naphthoquinone with phosphanes PPh_2R (R = Me, Ph, 2,5-$F_2C_6H_3$) lead to the betaines with phosphanium structure 1 (Chart 1) [5], which exhibit similar biological activity [6]. The similar reactions of polyfluorinated benzoquinones were not reported so far. The interaction of polyhaloquinones with phosphanes and phosphites has been attracting the attention of researchers for a long time [7]. It is, in particular, due to that this reaction, being carried out in the presence of water or alcohol, leads to phosphanium betaines 2 (Chart), which are of interest from the point of view of their electronic structure in terms of resonance of ketophosphorane 2A, ylide 2B and quinonebetaine structures 2C, 2D.

The reactions of chloranil, its less halogenated derivatives and bromanil with phosphanes led to betaines of type 2, if they are formed, as minor products but mainly phosphaniumphenolates 3 (Chart) formed by reduction of quinones [8–10]. Thus, chloranil was reported to react with PPh_3 [8] and $P(NEt_2)_3$ [9] to give only the corresponding phenolates 3 or their disproportion equivalents – the adducts of the respective triphenyl(4-[(triphenylphosphaniumyl)oxy]phenoxy)phosphanium and benzene-1,4-bis(olate) [8].

In reactions of chloranil with PEt_2Ph [10] and bromanil with $P(NEt_2)_2X$ (X = NEt_2, OEt) [9], alongside with prevailing reduction of quinones, phosphanodehalogenation and the subsequent hydrolysis of a primary reduction product occur to eventually lead to the corresponding betaines **2**. However, the mechanism of the reaction of quinones with organophosphorus compounds and structure of products, particularly in the case of preparing the compounds are internal salts such as betaines **2C**, **2D** and ylides **2B**, which are very sensitive to the polarity of the medium, can not be discussed without taking into account the influence of solvents. The nature of the solvent as a factor influencing the conversion halogenanils by the action of phosphorus compounds was not discussed.

In view of the above, in the present work the interaction of fluoranil **4** with PPh_3 in various solvents was studied and, unlike not only reduction [8–10], but also triphenylphosphanodefluorination was found to occur thus allowing (after hydrolysis of the

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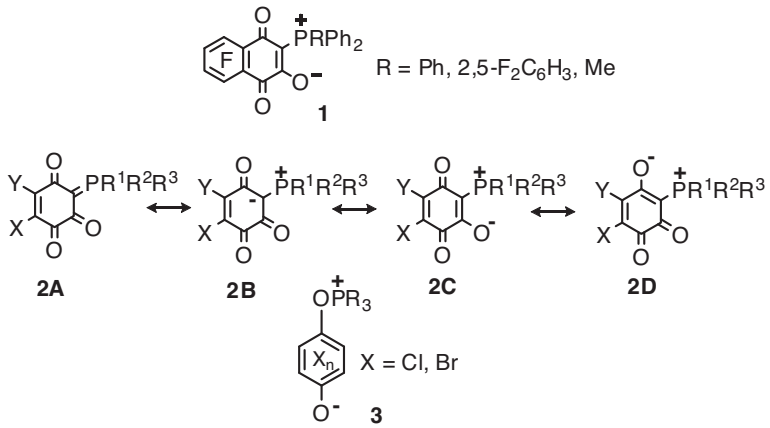


Chart 1. Structure **1**–**3**.

highly moisture-sensitive primary product registered by the ^{19}F and $^{31}P\{^1H\}$ NMR spectra) to prepare the corresponding (4,5-difluoro-2-oxido-3,6-dioxocyclohexa-1,4-dien-1-yl)triphenylphosphanium **5**. Analogous reaction for 2-X-trifluoro-1,4-benzoquinones (X = Cl, Me, OMe) were revealed. Besides, the possibility involving the primary triphenylphosphanodefluorination products in situ in the reactions with nucleophiles (aromatic amines) was demonstrated to give highly functionalized derivatives of benzoquinone.

2. Results and discussion

2.1. Reaction of fluoranil with PPh_3

By analogy with the literature data reactions were carried out in C_6H_6 [8–10] and more polar solvents too (anhydrous ethers, Et_2O, THF, dioxane, as well as MeOH, aq. dioxane and Me_2SO). The product distributions and structures were inferred from NMR (ESI[2] Supporting Table 1 and Table 2) and XRD data (ESI[2] Supporting Table 3).

2.1.1. Reaction in C_6H_6

The interaction of quinone **4** with PPh_3 (1:1) resulted after quenching by water in the solution and the precipitate. According to the ^{19}F and $^{31}P\{^1H\}$ NMR spectra, the solution contained (4,5-difluoro-2-oxido-3,6-dioxocyclohexa-1,4-dien-1-yl)triphenylphosphanium **5** (discussion of its structure in terms of the **2A–D** resonance see below Section 2.3) (~30% NMR yield, 19% isolated yield, here and hereinafter, per initial quinone **4**) and triphenylphosphaneoxide **6** (~50% NMR yield) (Scheme 1). The structure of betaine **5** was proved by the XRD analysis (see ESI[2] Supporting Figure 1).

The formation of betaine **5** is reasonably explained by the primarily occurring phosphanodefluorination of quinone **4** to give salt **7** which can reversibly turn into triphenyl(3,4,6,6-tetrafluoro-2-oxido-5-oxocyclohexa-1,3-dien-1-yl)phosphanium **8** and quinone **9**, and the subsequent hydrolysis of compounds **7**–**9** (compare [8–10]). The regioselectivity of hydrolysis reflected by structure of **5** is believed to be caused by the resonance charge distribution in the cation of salt **7**, through intermediacy of which hydrolysis of **8** and **9** can proceed also.

To experimentally prove this reaction pathway, the reaction of **4** with PPh_3 was carried out in carefully dried C_6H_6 in an atmosphere of dry argon and right after reagents mixing the signals were found out in the ^{19}F and $^{31}P\{^1H\}$ NMR spectra of a solution thus formed which are fairly compatible with the structure of the putative betaine **8** alongside with the signals belonging to triphenyldifluorophosphorane **10**. Thus, in the NMR ^{19}F spectrum (see ESI[2] Supporting Chart) of betaine **8** displayed three multiplets at δ_F −74.3 ppm (ddd, 2F, $^3J_{FP}$, $^4J_{FF}$ ~7, $^5J_{FF}$ = 3 Hz; CF_2), that is in line with data [11a,b] reported for α,α-difluoroketones, −125.0 ppm (ddt, 1F, $^4J_{FP}$ = 13, $^3J_{FF}$ = 10 and $^5J_{FF}$ = 3 Hz; F^3) and −154.1 ppm (dt, 1F, $^3J_{FF}$ ~10, $^4J_{FF}$ ~7 Hz; F^4). The phosphorane **10** resonance was observed at δ_F −39.1 ppm (d, 1F, $^1J_{FP}$ = 665 Hz). In the $^{31}P\{^1H\}$ NMR spectrum of the solution the signals at δ_P 15.9 ppm (dtd, 1P, $^4J_{PF}$ ~13, $^3J_{PF}$ ~7, $^5J_{PF}$ ~2 Hz) and −54.5 ppm (t, 1P, $^1J_{PF}$ = 665.0 Hz) belonged to compounds **8** and **10**, respectively. The observed phosphorane **10** NMR characteristics correspond to [12]. The signals of betaine **5** were observed along with the signals of **8** that testified the latter was undergone extremely easy hydrolysis (Scheme 1) with atmospheric moisture without the addition of water.

According to Scheme 1, formation of **10** (as well as **6**) can testify for the reduction of quinone **4** by PPh_3 to compete with its phosphanodefluorination which is suggested, by analogy with rationale of the similar chloranil transformation [8], to lead to phosphanium–zwitterion **11** or its disproportionation derivative **11a**. Thus two equivalents of fluoride anion are needed for formation of one equivalent **10**, but only the salt **7** being its source. Accordingly, two equivalents of the cation of this salt should bind with one equivalent of the tetrafluorohydroquinone dianion **13**. Since there were no signals in the NMR spectra of the solution which could be assigned to any adduct formed by these species, it was reasonably expected to be contained in the precipitate formed in the reaction.

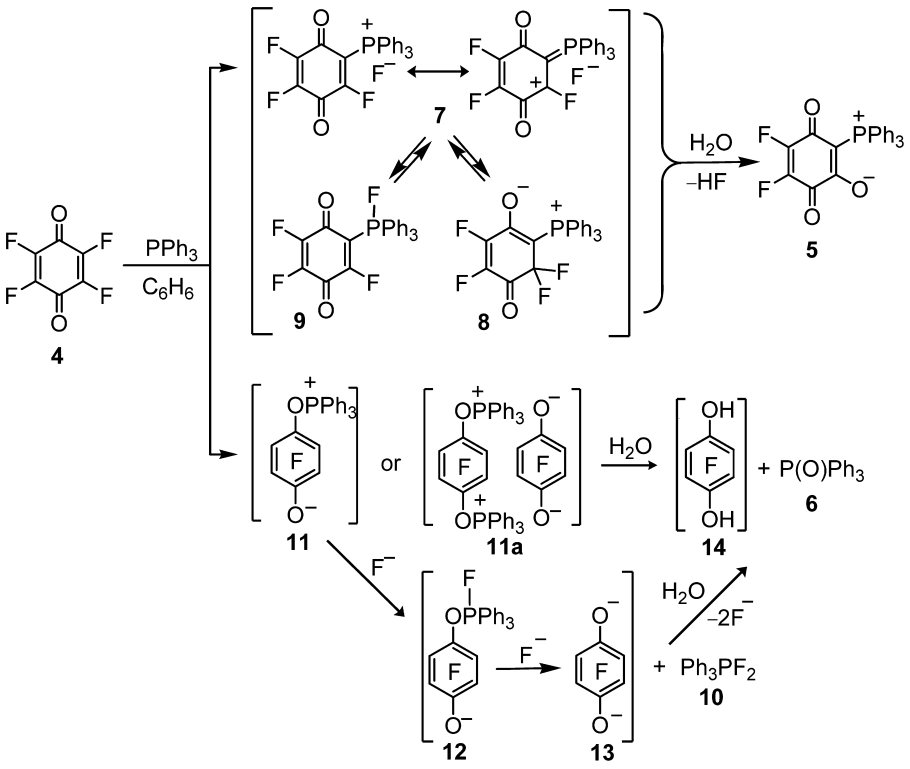
The ratio of compound **5** to the sum **6** and **10** determines the contribution of phosphanodefluorination and reduction.

According to the NMR data the benzene solution contained **5** (27% NMR yield) and **6** (25% NMR yield).

The amount of precipitate was ~55% from the initial compounds, what could point to a significant contribution of the reaction of reduction quinone **4**. The ^{19}F and $^{31}P\{^1H\}$ NMR spectra of the precipitate solution in Me_2SO displayed the presence of a small amount of betaine **5** (~1% yield per initial quinone **4**), **6** (~1% yield per initial PPh_3) and not identified products. Thus, the total yields of betaine **5** and **6** were 28% and 26% respectively. Along with this in the ^{19}F NMR spectrum the unresolved signal was observed at −163.7 to −156.0 ppm which is expected for tetrafluorohydroquinone **14** (−164.7 ppm [13]) or some of its derivatives. The above data testifies that in the reaction with PPh_3 quinone **4** undergoes triphenylphosphanodefluorination and reduction in a ~1:1 ratio.

An addition of a 0.6-equivalent of aniline **15** to a solution prepared by reaction of quinone **4** and PPh_3 gave an additional

[2] Electronic Supplementary Information (ESI) available: See http://dx.doi.org/10.1016/j.jfluchem.2015.08.018.



Scheme 1. Reaction of **4** with PPh_3.

evidence for formation of the betaine **8**; according to NMR data [4-fluoro-2-oxido-5-oxo-3-(phenylamino)-6-(phenylimino)cyclohexa-1,3-dien-1-yl]triphenylphosphanium **16** was formed (29% isolated yield) (Scheme 2).

Keeping of the benzene solution of fluoranil **4** and PPh_3 for 3 h with following treatment by a 2.0 fold excess of aniline **15** resulted in the formation of betaine – [4-fluoro-2-oxido-3,6-dioxo-5-(phenylamino)cyclohexa-1,4-dien-1-yl]triphenylphosphanium **17** (27% isolated yield) (Scheme 2), which is product of the reaction between aniline **15** and betaine **5**, the latter is formed, apparently, as a result of hydrolysis of **7**–**9** by atmospheric moisture or including residual moisture in aniline. The structures of betaines **16** and **17** were solved by XRD analysis (see ESI[2] Supporting Figure 2).

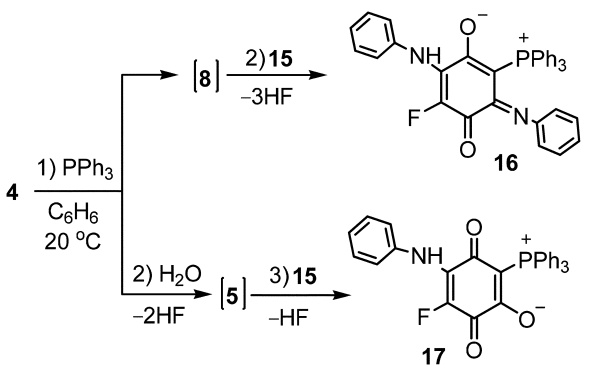
2.1.2. Reactions in anhydrous ethers (Et_2O, THF, dioxane) and aq. dioxane

The reaction of **4** with PPh_3 (1:1) under dried argon gives a solution and a precipitate in all ethers. According to ^{19}F NMR data, the solutions contained betaines **8** and **5** (1.0:1.3, in Et_2O; and 1.0:0.1–1.0, in THF and dioxane), as well as **10** in a (0.5–1.0)-fold amount with respect to the sum of betaines. In the ^{19}F NMR spectra the signal was observed belonging with a high probability to hydrogen fluoride (singlet at δ_F −186.6 ppm in Et_2O, −193.5 ppm in THF, and −192.3 ppm in dioxane) (cf. δ_F −26.9 ppm reported for liquid HF with C_6F_6 as external standard, δ_F = −162.9 ppm with respect to $CFCl_3$ [14]).

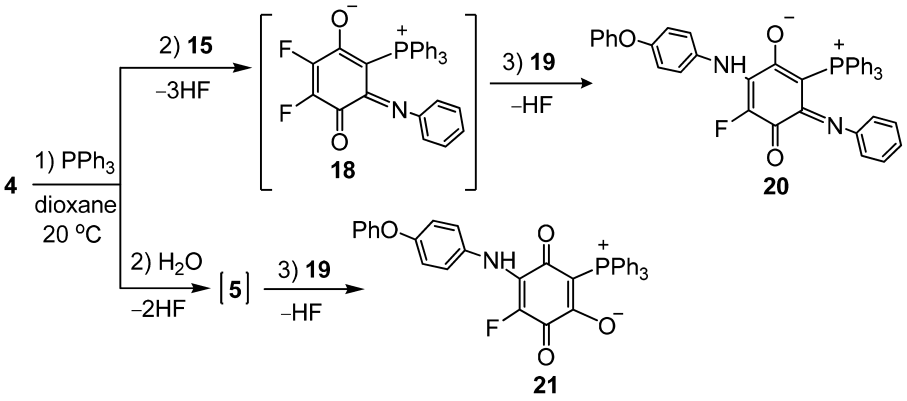
In all cases the amount of precipitates were ~30% from the initial compounds, which is two times less in comparison with the reaction in anhydrous C_6H_6. The NMR data of the precipitate solutions in Me_2SO displayed the presence of not identified products, possibly, the derivatives of tetrafluorohydroquinone.

It is possible that the betaine **5** partly formed due to the interaction of the salt **7** with ethers as O-centered nucleophile, followed by cleavage of C–O bonds of $-O^+Alk_2$ fragment of adduct by fluoride ion. The probability of such transformations is high due to the similar reactions of hexafluoro-1,4-naphthoquinone with PPh_3 in MeOH [5]. However, in general, betaine **5**, apparently is formed by the hydrolysis of compounds **7**–**9**, the moisture is penetrated into solution with the addition of PPh_3 to **4**. This is evidenced by the fact that, according to ^{19}F NMR data in carefully dried dioxane in dry-box, contained betaine **8** with a small trace of betaine **5** (~10%).

In order to determine the sequence in which fragments of aniline **15** included in the structure of betaine **16**, to a mixture of compounds **8** and **5** in dioxane (~1.3:1.0, according to ^{19}F NMR spectrum) was added 0.2 equivalent of aniline **15**. In addition to signals of betaine **5** the spectrum contained two equal intensity multiplets at δ_F −132.1 ppm (dd, 1F, $^4J_{FP}$ ~13, $^3J_{FF}$ ~10 Hz) and −151.5 ppm (d, 1F, $^3J_{FF}$ ~10 Hz). In the $^{31}P\{^1H\}$ NMR spectrum signal at δ_P 13.2 ppm (d, $^4J_{PF}$ ~13 Hz) was observed. This NMR characteristics are consistent with the presented structure of betaine – [3,4-difluoro-2-oxido-5-oxo-6-(phenylimino)cyclohexa-1,3-dien-1-yl]triphenylphosphanium **18**. At the same time, there



Scheme 2. Reaction of **4** with PPh_3 and following treatment of the benzene solution with aniline **15**.



Scheme 3. Reaction of **4** with PPh_3 and following treatment with anilines **15** and **19** in dioxane.

was no signal of betaine **8** with the doubled intensity in the range from −75.0 to −74.0 ppm (see ESI[2] Supporting Chart).

The attempt to isolate betaine **18** is failed, but the addition of an excess of 4-phenoxyaniline **19** to the reaction mixture gives a new compounds – {4-fluoro-2-oxido-5-oxo-3-[(4-phenoxyphenyl)amino]-6-(phenylimino)cyclohexa-1,3-dien-1-yl}triphenylphosphanium **20** and {4-fluoro-2-oxido-3,6-dioxo-5-[(4-phenoxyphenyl)amino]cyclohexa-1,4-dien-1-yl}triphenylphosphanium **21**. Betaines **20** and **21** were isolated with 18% and 26% yields respectively by TLC (Scheme 3). The structure of **21** is established by the XRD analysis (see ESI[2] Supporting Figure 3).

Conducting the reaction in aq. dioxane leads to a noticeable increase in output of products of phosphanodefluorination, apparently, in consequence of increasing contribution of this direction of reaction in the total result of the interaction in comparison to reduction. The interaction of **4** with PPh_3 (1:1) in aq. dioxane (~1:20) system resulted in solution and precipitate. According to the NMR data the solution contained compounds **5** and **6** (~60% and ~24%). Betaine **5** was isolated with 24% yield that currently makes conducting the reaction in these conditions the most convenient method of synthesis this compound. The resulting precipitate (the amount of precipitate was ~13% from the initial compounds) contained, as described previously [15] pure betaine – [2,4-dioxido-3,6-dioxo-5-(triphenylphosphaniumyl)cyclohexa-1,4-dien-1-yl]triphenylphosphanium **22** (9% isolated) (Scheme 4). In the same solvent with a molar ratio of **4** with PPh_3 = 1.0:3.0, betaine **22** was isolated with 53% yield. In the reaction of betaine **5** with PPh_3 (1.0:2.5) in dioxane, betaine **22** was isolated with 51% yield (Scheme 4). This testifies that betaine **5** is a precursor of bis-betaine **22**.

However, there cannot be discarded the path including phosphanodefluorination salt **7** with the formation of salt **23** and its following hydrolysis. The obtained result means that during phosphanodefluorination of **7**, nucleophilic attack was not aimed at neighboring position of Ph_3P^+ group but at a fragment of –CF=CF– bond. Given that during the reaction the reagent enters the cationic state, such a change of orientation could be due to steric and electrostatic hindrances of Ph_3P^+ group, which prevent the attack at neighboring position by bulky PPh_3 reagent. Thus, phosphanodefluorination is carried out at the position of –CF=CF– bond, which associates with more acceptor of the two carbonyl groups of salt **7**, due to the fact that in the *meta*-position to it stands cationic substituent Ph_3P^+.

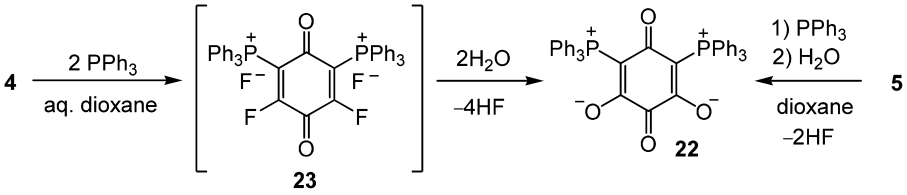
2.1.3. Reactions in Me_2SO

Initially in the NMR ^{19}F spectrum of a solution of quinone **4** in Me_2SO there are along with singlet at δ_F −143.9 ppm, which belong to **4**, two multiplets at −161.1 and −136.5 ppm. The location and structure of these signals correspond to those of fluorine atoms $F^{2,6}$ and $F^{3,5}$, respectively. According to data of polyfluorinated cyclohexa-2,5-dien-1-ones [16] we suggest formation of cyclohexadienone **24** – the product of addition Me_2SO to the carbonyl group quinone **4** (Scheme 5), the ratio of **4** and supposed **24** is ~3:1. In this regard, we can not exclude that the salt **7** is formed only (or not so much) directly from the quinone **4**, but in a roundabout way – through its reversible transformation into cyclohexadienone **24** and triphenylphosphanodefluorination last (Scheme 5).

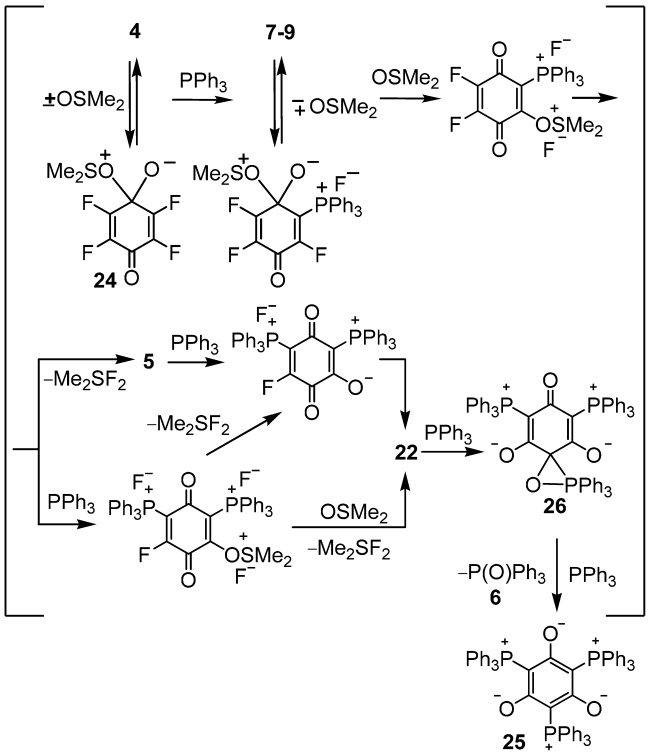
The interaction of **4** with PPh_3 (1:1) in Me_2SO resulted after quenching water in the solution. A precipitate was not formed. According to the NMR data this solution contained betaines **5**, **22**, **25** (~40%, 2% and 20%, respectively) and **6** (~10%). The ratio of triphenylphosphanodefluorination/reduction of **4** is ~6:1 ratio. The interaction of **4** with 6 equivalent of PPh_3 in Me_2SO under dried argon gave a mixture, from which known [15] betaine – triphenyl[2,4,6-trioxido-3,5-bis(triphenylphosphaniumyl)phenyl]-phosphanium **25** was isolated with 21% yield. A probable path of his formation, as shown in Scheme 5, involves the accession of PPh_3 to the bis-betaine **22** at a more acceptor of its two carbonyl groups and subsequent deoxygenation of arising betaine – [2,2,2-triphenyl-1,2λ^5-oxaphosphirane (4,8-dioxido-6-oxo-2,2,2-triphenyl-7-(triphenylphosphaniumyl)-1-oxa-2λ^5-phosphaspiro[2.5]octa-4,7-dien-5-yl]triphenylphosphanium) **26**. The role of oxygen-centered nucleophile, possibly, executes a solvent (Scheme 5).

2.1.4. Reactions in MeOH

As described above for solution in Me_2SO, in the NMR ^{19}F spectrum of **4** in MeOH along with singlet at δ_F −143.9 ppm, which belong to **4**, there are two multiplets at −157.7 and −136.9 ppm of



Scheme 4. Reaction of **4** with PPh_3 in dioxane – H_2O.



Scheme 5. Reaction of fluoranil **4** with PPh_3 in Me_2SO.

cyclohexadienone **27**, which is the product of MeOH conjunction to the carbonyl group of **4** (Scheme 6). After exposure of the solution 1 h, quinone **4** was returned quantitatively. In a concentration range of 0.12–1.04 mol/l the ratio of compounds **4** and **27** is about ~7:1 and remaining constant over 14 days, up to ~40% conversion of quinone **4** into 2-methoxy-trifluoro-1,4-benzoquinones **28** (infrared spectrometry data and NMR ^{19}F characteristics correspond to [13,17]).

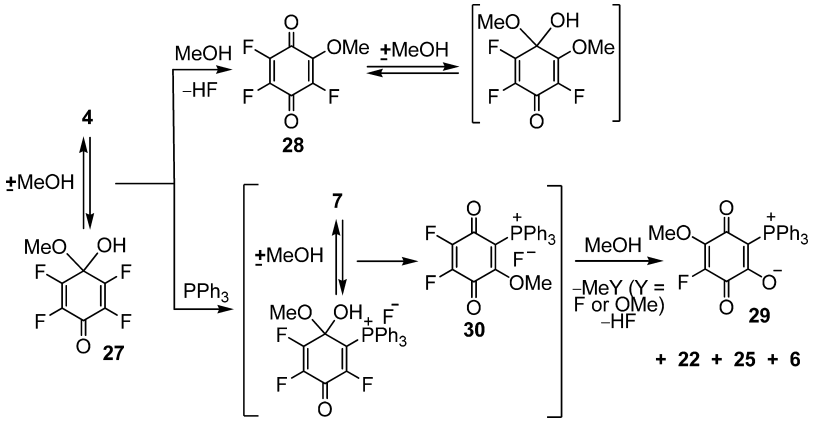
Previously [18] it was reported that **4** reacts with MeOH at room temperature for a long time (strictly not specified) with formation of 2,5-dimethoxy-3,6-difluoro-1,4-benzoquinone. Regioselectivity of fluoride substitution could be reasonable explain to the deactivation of position 3 in the primary product of methoxydefluorination **28** due to π-donor effect of 2-MeO-group. The latter, in addition, reduces electron-acceptor effect of conjugated with her 4-C=O group, resulting what secondary substitution take place at the 5 position of the fragment –CF=CF–, which paired with more acceptor 1-C=O group. The interaction of **4** with MeOH for 30 min at 100 °C resulted to **28** [17]. It is similar to the above reaction in Me_2SO. The equilibrium between **4** and **27** has uncertainty in the transition from **4** to the product of its nucleophilic defluorination, in this case the quinone **28** (Scheme 6).

The interaction of **4** with PPh_3 (1:1) in MeOH at room temperature 1 h, according to the NMR data resulted in the mixture of mono-, di- and trisubstituted products. The precipitate was not formed. Reaction mixture contained betaine – (4-fluoro-5-methoxy-2-oxido-3,6-dioxocyclohexa-1,4-dien-1-yl)triphenylphosphanium **29**, betaines **22** and **25** (~35%, 18% and 7%, respectively). The fluoranil **4** and **6** (~10% and 30%, respectively) were present too. Quinone **4** with PPh_3 undergoes triphenylphosphanodefluorination and reduction in a ~2:1 ratio. In similar experiment with a larger scale the reaction of **4** with PPh_3 (1:1) gave a precipitate, which was a pure betaine **29** with 49% yield. The structure of betaine **29** was proved by the XRD analysis (see ESI[2] Supporting Figure 4).

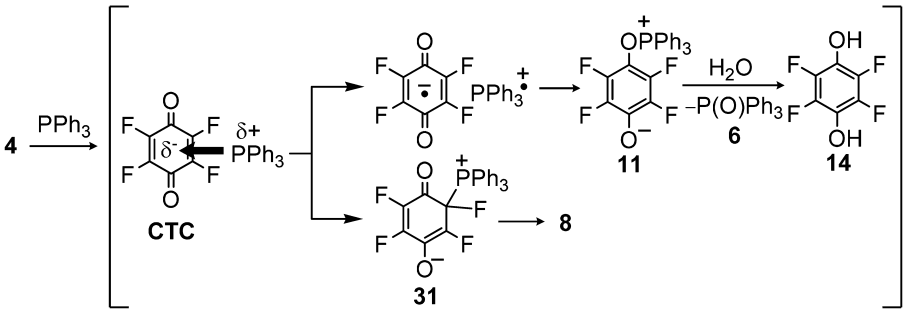
Formally, obtained result does not provide the information about the sequence of phosphano- and methoxydefluorination on the path from **4** to **29**. However, because **4** practically does not undergo methoxydefluorination over time 1 h at the room temperature, in the presence of PPh_3 it is completely converted into betaine **29** and other di- and trisubstituted products. It can be concluded that first occur phosphanodefluorination of **4** (or its adduct **27** with MeOH) with the formation of salt **7**. Methoxydefluorination of this salt (or it adduct with MeOH) gives the quinone **30**, which undergoes methoxydefluorination and demethylation (the sequence of these transformations is unclear) (Scheme 6).

The ^{19}F NMR data indicate on a high probability of the cyclohexadienones formation as a result of addition of solvent (Me_2SO, MeOH) to the carbonyl group quinone **4**. There are two possible ways of realization of nucleophilic dehalogenation of **4**: either directly in the quinone or in the cyclohexadienone, which is in the equilibrium with **4** with the subsequent regeneration of the quinone structure. Polyfluorinated cyclohexadienones very easily undergo nucleophilic defluorination [19]. It is possible that cyclohexadienone even more active than quinone to nucleophile addition to carbon–carbon double bond, as in this case the quinone lost its conjugation with two carbonyl groups, and in case of cyclohexadienone – with only one. In each case the question of which way proceeds a reaction of nucleophilic substitution in quinone, requires special investigation.

Fluoranil **4** with PPh_3 in various solvents undergoes phosphanodefluorination and reduction unlike chloranil, which undergoes only reduction [8–10]. The absence of phosphanodefluorination for chloranil was explained by steric hindrance of the nucleophilic attack on –CCl=CCl– bond and high oxidation potential of chloranil [8]. In the case of fluoranil **4** along with reduction is implemented



Scheme 6. Reaction of **4** with PPh_3 in MeOH.



Scheme 7. Formation of CTC in reaction of **4** with PPh_3.

phosphanodefluorination, suggests that from these two reasons, the first is more important, besides this is supplemented by a greater electrophilicity of the carbon atom of C–F bond compared to C–Cl bond. The role of oxidation potential of the quinone detected by comparing the presented above yield of betaine **5** with almost quantitative yield of its analog in the reaction of hexafluoro-1,4-naphthoquinone with PPh_3 [5].

The comparison of the results of the interaction of quinone **4** with PPh_3 in C_6H_6 and aq. dioxane indicates the tendency for increment of phosphanodefluorination in its competition with the reduction with an increase in the polarity of the medium. This effect corresponds to the fact that the system undergoes a larger polarization during phosphanodefluorination than during reduction. Previously two points of view on the mechanism of reduction of halogenated quinones with PPh_3 were expressed. Firstly, it is a direct nucleophilic attack at oxygen atom with the formation of betaine **11** or **11a** [8]. However, the reported effect of solvent polarity does not correspond to this conception, because during the formation of betaine **11** system undergoes, as it can be assumed, the greater polarization than during the nucleophilic attack on the carbon–carbon double bond with the formation of intermediate **31** (Scheme 7). By analogy with the mechanism of interaction of chloranil with trialkylphosphite [20] we assume that the first and common intermediate for the both competing reaction is a complex with charge transfer (CTC) between the quinone **4** and PPh_3. The decrease in products of reduction with increasing polarity of the solvent can be explained by the fact that during this transformation the transition from CTC to radical-anion is accompanied by delocalization of the negative charge, while the transition from the CTC to the intermediate of phosphanodefluorination **31** is accompanied by its localization (Scheme 7).

In addition, the effect of medium polarity on competition of the two submitted transformations are not in consistent with the views of the authors [10] on a smaller division of charges of opposite sign in the transition state of phosphanodefluorination compared to the transition state of reduction.

2.2. Interaction of 2-X-trifluoro-1,4-benzoquinones (X = Cl, Me, OMe) with PPh_3 in anhydrous C_6H_6 and dioxane

The interaction of all indicated quinones with PPh_3 gave a solution and a precipitate, which, similar to those obtained from the fluoranil **4**, supposed to contain the products of reduction, particularly in the form of adducts, with products of triphenylphosphanodefluorination. A common feature of these reactions is triphenylphosphanodefluorination at positions 5 and 6 in depending on the nature of the substituent X.

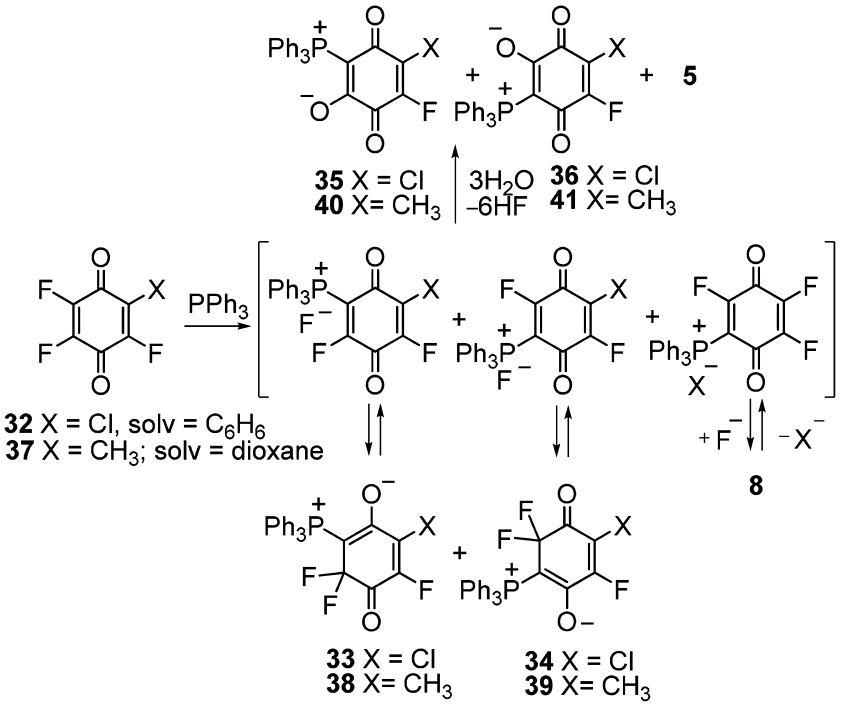
The interaction of 2-chloro-trifluoro-1,4-benzoquinone **32** with PPh_3 (1:1) in carefully dried C_6H_6 in an atmosphere of dry argon at the room temperature gave a solution and a precipitate. According to the NMR data solution contained analogs of betaine **8**, the products of phosphanodefluorination of quinone **32** – isomeric betaines (3-chloro-4,6,6-trifluoro-2-oxido-5-oxocyclohexa-1,3-dien-1-yl)triphenylphosphanium **33**, (4-chloro-3,6,6-trifluoro-2-oxido-5-oxocyclohexa-1,3-dien-1-yl)triphenylphosphanium **34** respectively, and the product of chlorine substitution – betaine **8** (Scheme 8). Besides initial quinone **32** and **10** (14% and ~77%, respectively) (Scheme 8) and corresponding to the hydrolysis betaines – (5-chloro-4-fluoro-2-oxido-3,6-dioxocyclohexa-1,4-dien-1-yl)triphenylphosphanium **35** and (4-chloro-5-fluoro-2-oxido-3,6-dioxocyclohexa-1,4-dien-1-yl)triphenylphosphanium **36** and **5** present in the reaction mixture too. The ratio of isomeric betaines is (**33** + **35**):(**34** + **36**):(**8** + **5**) = 12:1:3, which are determined by the attack of PPh_3 at positions 6, 5 and 2 and show a much higher activity of positions 6 and 2 compared to position 5 in regard to attack of nucleophile. Quinone **32** with PPh_3 undergoes triphenylphosphanodefluorination and reduction in a (**33** + **34** + **35** + **36** + **8** + **5**):(**10**) = ~1:10 ratio.

In the NMR ^{19}F spectrum betaines **33** and **34** displayed two multiplets each with 2:1 intensity ratio at δ_F −73.5 ppm (dd, 2F, $^4J_{FF}$, $^3J_{FP}$ ~7 Hz, CF_2), −122.5 ppm (t, 1F, $^4J_{FF}$ ~7 Hz, F^4) for betaine **33** and at δ_F −71.9 ppm (d, 2F, $^3J_{FP}$ ~7 Hz, CF_2), −100.7 ppm (d, 1F, $^4J_{FP}$ ~14 Hz, F^3) for betaine **34**. In the $^{31}P\{^1H\}$NMR spectrum of the benzene solution the signals belonged to betaines **33** and **34** were at δ_P 16.0 (dt, $^3J_{PF}$ ~7, $^5J_{PF}$ ~ 1 Hz) and 14.0 ppm (dt, $^4J_{PF}$ ~14, $^3J_{PF}$ ~7 Hz) respectively. The ^{19}F and $^{31}P\{^1H\}$ NMR spectra of solution after 24 h without isolation from moisture in the air displayed only the presence of betaines **35**, **36**, **5** and compound **6** (~5%, 1%, 1% and 77% yields, respectively). Betaine **35** was isolated with 3% yield. The structure of betaine **35** was proved by the XRD analysis (see ESI[2] Supporting Figure 4).

The amount of precipitate was ~33% from the initial compounds, which is less in comparison with the reaction of fluoranil **4** in anhydrous C_6H_6. The ^{19}F and $^{31}P\{^1H\}$ NMR spectra of the precipitate solution in Me_2SO displayed the presence of a small amount of betaine **35** (~1% yield per initial quinone **32**), **6** (~1% yield per initial PPh_3) and not identified products.

According to the ^{19}F and $^{31}P\{^1H\}$ NMR spectra of benzene solution and precipitate dissolved in Me_2SO a total yields of **35**, **36**, **5** and **6** are 6%, 1%, 1% and 78% respectively. The above data testifies that in the reaction with PPh_3 quinone **32** undergoes triphenylphosphanodefluorination and reduction in a ~1:10 ratio.

The interaction of quinone **32** with PPh_3 (1:1) in dried dioxane in dry-box under dried argon gave a solution and a precipitate. The ratio of isomeric betaines, which are determined by the attack of PPh_3 at 6, 5 and 2 positions, is (**33** + **35**):(**34** + **36**):(**8** + **5**) = 10:1:6 and also show a much higher activity of positions 6 and 2 compared to position 5 of quinone **32**. In the reaction mixture were present phosphorane **10** and initial quinone **32** (~63% and 16% yields, respectively) (Scheme 8). Quinone **32** with PPh_3 undergoes triphenylphosphanodefluorination and reduction in a (**33** + **34** + **35** + **36** + **8** + **5**):(**10**) = 1:2 ratio. Betaine **35** was isolated with 14% yield. In the NMR ^{19}F spectrum betaine **36** displayed



Scheme 8. Reactions of quinones **32** and **37** with PPh_3.

one singlet signal at δ_F −117.1 ppm (F^5), and in the $^{31}P\{^1H\}$ NMR spectrum – singlet at δ_P 15.1. Also the signal was observed belonging with a high probability to hydrogen fluoride (singlet at δ_F −189.6 ppm).

The amount of precipitate in that reaction was ~14% from the initial compounds. The ^{19}F and $^{31}P\{^1H\}$ NMR spectra of the precipitate solution in Me_2SO displayed the presence of a small amount of **35** (~1% yield per initial quinone **32**), **6** (~1% yield per initial PPh_3) and not identified products.

According to the ^{19}F and $^{31}P\{^1H\}$ NMR spectra of dioxane solution and precipitate dissolved in Me_2SO a total yields of betaines **35**, **36 and 5** are 21%, 2% and 11% respectively. The above data testifies that in the reaction with PPh_3 quinone **32** undergoes triphenylphosphanodefluorination and reduction in a ~1:2 ratio.

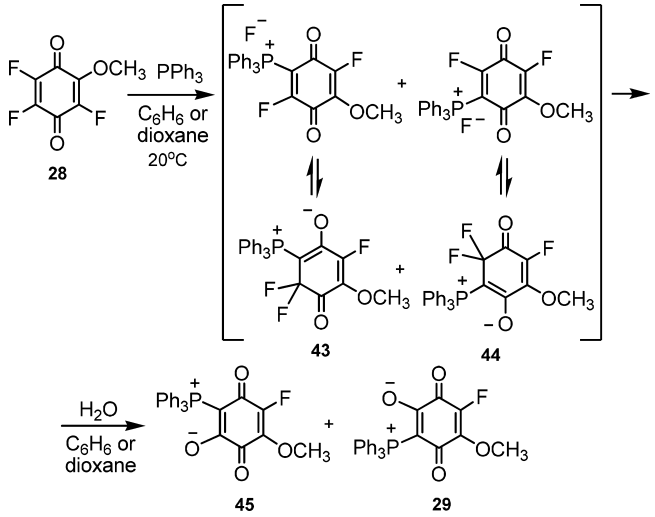
Product ratios of reaction quinone **4** with PPh_3 suggests that the replacement of the fluorine atom with a chlorine at the transition from quinone **4** to quinone **32** appreciably discriminates the position 5 in competition with position 6 in regard to attack of nucleophile. The obvious reason for this is a weaker electron-donor resonance effect of chlorine atom in comparison with the fluorine atom, that makes 4-C=O group a stronger acceptor compared to 1-C=O group. The presence of **10** and, correspondingly, isolation the product of its hydrolysis – **6**, indicate a significant contribution the process of reduction of initial quinone in the total result of the interaction.

The interaction of 2-methyl-trifluoro-1,4-benzoquinone **37** with PPh_3 (1:1) in dried dioxane in dry-box under dried argon gave a solution and a precipitate. According to NMR data the solution contained betaines triphenyl(4,6,6-trifluoro-3-methyl-2-oxido-5-oxocyclohexa-1,3-dien-1-yl)phosphanium **38** and triphenyl(3,6,6-trifluoro-4-methyl-2-oxido-5-oxocyclohexa-1,3-dien-1-yl)phosphanium **39** (2.0:1.0 respectively) and also, the products of their hydrolysis – (4-fluoro-5-methyl-2-oxido-3,6-dioxocyclohexa-1,4-dien-1-yl)triphenylphosphanium **40** and (5-fluoro-4-methyl-2-oxido-3,6-dioxocyclohexa-1,4-dien-1-yl)triphenylphosphanium **41** (21:1). The ratio (**38** + **40**):(**39** + **41**) = 13:1 indicate a much higher activity of position 2 compared to position 3 of quinone **37** in regard to attack of nucleophile, obviously, for the reason similar to that discussed above for the quinone **32**. The ratio of triphenylphosphanodefluorination (**38** + **39** + **40** + **41**) and reduction (**10**) is ~1:1. Also phosphorane **10** and initial quinone **37** were present (~40% and 8%, respectively) (Scheme 8).

In the ^{19}F NMR spectra the signal was observed belonging with a high probability to hydrogen fluoride (singlet at δ_F −183.9 ppm). In the NMR ^{19}F spectrum betaines **38** and **39** displayed two multiplets each with 2:1 intensity ratio at δ_F −74.6 ppm (br. s, 2F, CF_2), −130.7 ppm (br. s, 1F, F^4) for betaine **38** and at δ_F −74.8 ppm (br. s, 2F, CF_2), −103.9 ppm (dm, 1F, $^4J_{FP}$ ~15 Hz, F^3) for betaine **39**. In the $^{31}P\{^1H\}$ NMR spectrum of the dioxane solution the signals at δ_P 14.8 (br. s) and 15.4 ppm (dm, $^4J_{PF}$ ~15 Hz) belonged to betaines **38** and **39** respectively. In the NMR data of the dioxane solution betaine **41** displayed multiplet at δ_F −110.9 ppm (dq, $^4J_{FP}$ = 16.0 Hz, $^4J_{FH}$ = 3.1 Hz, F^5), and multiplet at δ_P 15.4 ppm (dm, $^4J_{PF}$ = 16.0 Hz) (NMR data of **40** see Supporting Table 1).

The ^{19}F and $^{31}P\{^1H\}$ NMR spectra of solution after 24 h without isolation from moisture in the air displayed only the presence of betaines **40**, **41** and **6** (~43%, 3% and 40%, respectively). After chromatography of solution on silica gel by a mixture of acetone – hexane (1:1) and then after second chromatography in ethyl acetate had been isolated betaine **40** and [4-fluoro-3-hydroxy-5-methyl-2-oxido-6-oxo-3-(2-oxopropyl)cyclohexa-1,4-dien-1-yl]triphenylphosphanium **42** with ~9% yield each. Apparently, betaine **42** is formed from **40** as a result of the addition one molecule of acetone. This is confirmed by the fact that betaine **40** (5% yield) was only obtained after chromatography of solution on silica gel by chloroform. Thus, the total yield of betaine **40** was 14%. The structure of betaines **40** and **42** was proved by the XRD analysis (see ESI[2] Supporting Figure 5).

The amount of precipitate in that reaction was ~24% from the initial compounds. The NMR data of the precipitate solution in Me_2SO displayed the presence of a small amount of betaine **40** (~4% yield per initial quinone **37**) and **6** (~7% yield per initial PPh_3). According to the ^{19}F and $^{31}P\{^1H\}$ NMR spectra of dioxane solution and precipitate dissolved in Me_2SO a total yields of betaines **40**, **41** and **6** are 47%, 3% and 47% respectively. The data testifies that



Scheme 9. Reactions of **28** with PPh_3 in C_6H_6 and dioxane.

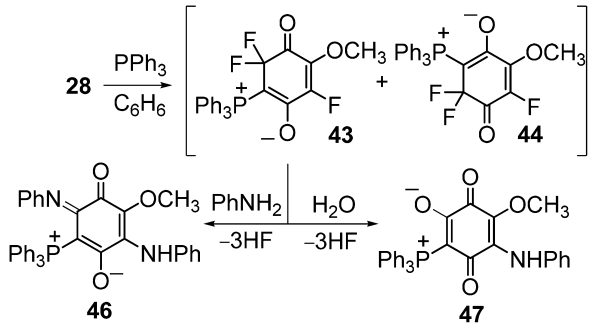
quinone **37** with PPh_3 undergoes triphenylphosphanodefluorination and reduction in a ~1:1 ratio.

The interaction of 2-methoxy-trifluoro-1,4-benzoquinone **28** with PPh_3 (1:1) in dried C_6H_6 in dry-box under dried argon also led to a precipitate formation. According to NMR data the solution contained triphenyl(3,6,6-trifluoro-4-methoxy-2-oxido-5-oxocyclohexa-1,3-dien-1-yl)phosphanium **43** and triphenyl(4,6,6-trifluoro-3-methoxy-2-oxido-5-oxocyclohexa-1,3-dien-1-yl)phosphanium **44** (4.0:1.0) and also, the products of their hydrolysis – (5-fluoro-4-methoxy-2-oxido-3,6-dioxocyclohexa-1,4-dien-1-yl)triphenylphosphanium **45** and **29** (17:1) (Scheme 9).

In the NMR ^{19}F spectrum betaines **43** and **44** displayed two multiplets each with 2:1 intensity ratio at δ_F −74.5 ppm (dd, 2F, $^3J_{FP}$ ~7, $^5J_{FF}$ ~3 Hz, CF_2), −125.7 ppm (dm, 1F, $^4J_{FP}$ ~14, $^5J_{FH}$ ~4, $^5J_{FF}$ ~3 Hz, F^3) for betaine **43** and at δ_F −74.7 ppm (dd, 2F, $^4J_{FF}$, $^3J_{FP}$ ~7 Hz, CF_2), −159.1 ppm (m, 1F, $^4J_{FF}$ ~7 Hz; F^4) for betaine **44**. In the $^{31}P\{^1H\}$ NMR spectrum of the benzene solution the signals at δ_P 15.8 (dt, $^4J_{PF}$ ~14, $^3J_{PF}$ ~7 Hz) and 15.7 ppm (t, $^3J_{PF}$ ~7 Hz) belonged to betaines **43** and **44** respectively. In the NMR ^{19}F spectrum of the C_6H_6 solution betaine **45** displayed multiplet at δ_F −132.9 ppm (dq, $^4J_{FP}$ = 14.0, $^5J_{FH}$ = 2.4 Hz, F^5), and in the $^{31}P\{^1H\}$ NMR spectrum – the signal at δ_P 14.5 ppm (d, $^4J_{PF}$ = 14.0 Hz) (NMR data for betaine **29** see Supporting Table 2).

The ratio (**43** + **45**):(**44** + **29**) = 4:1 and (**29** + **43** + **44** + **45**):(**10**) = 4:1 differs significantly from mentioned above for quinones **4** and **37** and indicates in this case on a considerable predominance of phosphanodefluorination over the reduction. The probable reason for this change in the ratio of competing paths is the electron-donor effect of the methoxy group. The replacement of the fluorine atom with a methoxy group at the transition from quinone **4** to quinone **28**, appreciably reduces the tendency of the quinone to reduction but to a lesser extent discriminates the attack of nucleophile, at least to position 3, that conjugate with the most acceptor from two carbonyl groups of the quinone **28**.

After the addition of an excess of aniline **15** to a reaction mixture were obtained new compounds – [4-methoxy-2-oxido-5-oxo-3-(phenylamino)-6-(phenylimino)cyclohexa-1,3-dien-1-yl]triphenylphosphanium **46** and [4-methoxy-2-oxido-3,6-dioxo-5-(phenylamino)cyclohexa-1,4-dien-1-yl]triphenylphosphanium **47** (~7:1) (Scheme 10). Betaines **46** and **47** were isolated by TLC with 43% and 7% yields respectively and characterized. The structures of betaines **46** and **47** were established by XRD analysis (see ESI[2] Supporting Figure 6).



Scheme 10. Reaction of **28** with PPh_3 and following treatment of the benzene solution with aniline **15**.

The interaction of quinone **28** with PPh_3 (1:1) in dried dioxane in dry-box under dried argon gave a solution and a precipitate. According to NMR data the solution contained betaines **43** and **44** (2:1) and also, the products of their hydrolysis – betaines **45** and **29** (4:1) (Scheme 10). The ratio (**43** + **45**):(**44** + **29**) is 3:1. In the ^{19}F NMR spectra the signal was observed belonging with a high probability to hydrogen fluoride (singlet at δ_F −187.6 ppm) [14]. The ratio of triphenylphosphanodefluorination (**29** + **45** + **43** + **44**) and reduction (**10**) of **28** is 3:1.

The NMR data of solution after 24 h without isolation from moisture in the air displayed only the presence of betaines **45**, **29** and oxide **6** (~50%, 16% and 27%, respectively). The attempts to isolate individual betaines **45** and **29** by TLC failed, but after addition to a reaction mixture of an excess of aniline **15** were obtained betaine **47** and other not identified products.

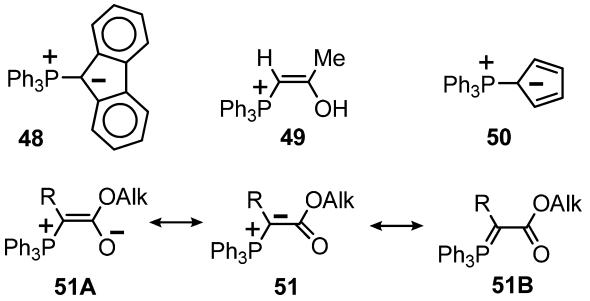
The amount of precipitate in that reaction was ~18% from the initial compounds. The NMR data of the precipitate solution in Me_2SO displayed the presence of a small amount **6** (~3% yield per initial PPh_3) and not identified products.

According to the NMR data of dioxane solution and precipitate dissolved in Me_2SO total yields of betaines **45**, **29** and **6** are 50%, 16% and 30% respectively. The above data testifies that quinone **28** with PPh_3 undergoes triphenylphosphanodefluorination and reduction in a ~2:1 ratio.

2.3. The NMR spectra and structures of betaines

NMR spectral characteristics of the synthesized compounds in this work are presented in Supporting Table 1 and Table 2 and fully meet their structures. Bis-betaine **22** and tris-betaine **25** were synthesized previously by other methods [15], and their $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data in the cited paper, fully correspond to those samples produced by us. The structure of betaines **5**, **16**, **17**, **20**–**22**, **25**, **29**, **35**, **40**, **42**, **46**, **47** were solved by XRD analysis.

It is of interest to analyze the NMR data with the aim to shed a light on the structure of betaines **5**, **16**, **17**, **20**–**22**, **25**, **29**, **35**, **40**, **42**, **46**, **47** in the context of canonical resonance structures **2A**–**2D** (R_{1-3} = Ph). Previously the authors [15] made a conclusion about the prevalence of quinone-betaine resonance structure **2C** for **22**. This conclusion was based on the fact, that in the NMR $^{13}C\{^1H\}$ spectrum of bis-betaine **22** the "carbonyl" atoms $C^{3,6}$ have downfield shifts to the signals of "enolate" atoms $C^{2,4}$. However, the assignment of signals does not seem to be a definite. Thus, a signal at δ_C 186.9 ppm was qualified as a triplet with a J_{CP} = 5.3 Hz coupling constant and by combination of these characteristics was assigned to C^6. But, in our case in the NMR $^{13}C\{^1H\}$ spectrum bis-betaine **22** displayed a triplet signal with the similar $^2J_{CP} \sim {}^4J_{CP}$ 5.1 Hz coupling constants, and on this basis shall be assigned to $C^{2,4}$. In work [15] a triplet signal at δ_C 184.4 ppm with J_{CP} = 14.5 Hz coupling constant and a singlet signal at 175.2 ppm were assigned to C^3 and $C^{2,4}$, respectively. But, in our case in the NMR $^{13}C\{^1H\}$



Scheme 11. The structures of ylides **48**–**51**.

spectrum of bis-betaine **22** a triplet signals at δ_C 184.3 and 175.1 ppm with $^2J_{CP}$ = 14.3 and $^3J_{CP}$ = 1.6 Hz coupling constants were assigned to C^6 and C^3, respectively. Downfield location of signals at δ_C 186.9 and 184.3 ppm may be due to a significant contribution of *ortho*-quinoid resonance structure **2D**, the assignment of the latter to C^6 based on the high value of coupling constant $^2J_{CP}$ 14.3 Hz (cf. $^2J_{CP}$ 12.7 Hz for C^6 in case of betaine **5**). In the $^{31}P\{^1H\}$ NMR spectrum there is a singlet signal at δ_P 13.4 ppm (cf. δ_P 13.8 ppm in [15]).

The structure of betaine **25** was justified by the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data that is in line with data reported in [15]. Thus, a singlet signal at δ_C 184.1 ppm (cf. δ_C 184.4 ppm in [15]) was assigned to $C^{2,4,6}$. A signal at δ_C 74.4 ppm, dm, $^1J_{CP}$ 118.0 Hz (cf. at δ_P 74.4 ppm, dt, $^1J_{CP}$ 116.0 and $^4J_{CP}$ 9.9 Hz in [15]) was assigned to $C^{1,3,5}$. In the $^{31}P\{^1H\}$ NMR spectrum there is a singlet signal at δ_P 13.4 ppm (cf. δ_P 13.7 ppm in [15]).

In this regard, to determine the electronic structure of the synthesized compounds in terms of resonance **2A** ↔ **2B** ↔ **2C**, **2D** seems more rational to consider the NMR characteristics of the fragments C–P. For ylides $Alk_3P^+–C^-HR$ (Alk = Me, Et; R = H, Me) the signals are located in the range δ_C from −14.0 to −2.0 ppm [21], but with decreasing of π-delocalization of the negative charge on the ylide C-atom, the signals shifts downfield (at δ_C 53.3 for **48** and 70.9 ppm for enol **49** [22]). The chemical shifts of the ylide C-atom approaches the values at δ_C 78.3 ppm for **50** and δ_C 117–119 ppm range for *ipso*-C-atom of phenyl ring of triphenylphosphanium cation $Ph_3P^+CH_2X$ (X = H, Me, Ph, OMe, Cl, etc.) [22] (Scheme 11).

The chemical shifts of the C–P bond associated with triphenylphosphanium group are in the range δ_C from 74.2 to 84.0 ppm in the series of isolated compounds (betaines **5**, **16**, **17**, **20**–**22**, **25**, **29**, **35**, **40**, **42**, **46**, **47**). That allows you to believe that their electronic structure is characterized by a predominant contribution of betaine resonance structures such as **2C** and **2D**.

That conclusion is in apparent contradiction with the location in the significantly strong field of analogous signals of structurally similar compounds **51** (at δ_C 29–33 ppm [22]). But can be rationally explained by the fact that in this case the electron-donor effect of alkoxy-group reduces the contribution of betaine structure **51A** in favor of structure **51B** (Scheme 11).

This conclusion is consistent with the change of values of coupling constant $^1J_{CP}$ in the series of compounds, which characterized by a gradual decrease in the negative charge on the "ylide" carbon atom: **48** – 128.7 Hz, **50** – 113.1 Hz [22], **5**, **16**, **17**, **20**–**22**, **25**, **29**, **35**, **40**, **42**, **46**, **47** – 103.4–118.0 Hz, **49** – 99.2 Hz [22].

3. Conclusions

The reactions of fluoranil **4** and its polyfluorinated analogs – 2-X-trifluoro-1,4-benzoquinones (X = Cl, Me, OMe) with PPh_3 were studied and, unlike the mentioned above for chloranil [8], not only reduction, but also triphenylphosphanodefluorination were found to occur.

We have also studied the effect of solvents (C_6H_6, Et_2O, THF, dioxane, MeOH, aq. dioxane and Me_2SO) on the competition of these transformations. It is shown that the use of more polar solvents, such as MeOH, aq. dioxane and Me_2SO, leads to an increase in products of phosphanodefluorination. The entry of solvent molecule into products of phosphanodefluorination of fluoranil was observed in MeOH.

The possibility of further nucleophilic modifications was demonstrated on the primary triphenylphosphanodefluorination products in the reactions with aniline and 4-phenoxyaniline to give highly functionalized benzoquinone derivatives.

4. Experimental

The NMR spectra were recorded with a Bruker AV 300 (^1H: 300.13 MHz, $^{13}C\{^1H\}$: 75.47 MHz, ^{19}F: 282.36 MHz, $^{31}P\{^1H\}$: 121.49 MHz) and AV-400 (^1H: 400.13 MHz, $^{13}C\{^1H\}$: 100.61 MHz) spectrometers in the respective deuterated solvents relative to the residual proton chemical shifts of acetone (δ_H 2.07 ppm, δ_C 29.80 ppm), chloroform (δ_H 7.25 ppm, δ_C 77.00 ppm) and Me_2SO-d_6 (δ_H 2.50 ppm) in ^1H NMR spectra, Me_4Si in $^{13}C\{^1H\}$ NMR spectra, external C_6F_6 (δ_F = −162.9 ppm) in ^{19}F NMR spectra, and H_3PO_4 in $^{31}P\{^1H\}$ spectra. High-resolution mass spectra (HRMS) were measured with a DFS Thermo scientific instrument (EI, 70 eV). The melting points were determined on an FP 900 Thermosystem microscope melting point apparatus (Mettler-Toledo International Inc., Zürich, Switzerland).

XRD data were obtained on a Bruker Kappa Apex II CCD diffractometer using φ, ω scans of narrow (0.5°) frames with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The structures were solved by direct methods and refined by full-matrix least-squares method against all F2 in anisotropic approximation using the SHELX-97 programs set [23]. The H atoms positions were calculated with the riding model. Absorption corrections were applied empirically using SADABS programs [24]. Compound **5** crystallizes with a solvating ½ C_6H_6 per unit. The structures of **17**, **35, 40** and **47** are formed by two crystallographically independent molecules, one of which is shown on Supporting Figures 2, 4, 5 and 6 respectively. The structure of **35** was refined as a 0.68:0.32(1) racemic twin. In the structure **47** one of phenyl ring is disordered over two positions with occupancy ratio of 0.528:0.472(6).

CCDC 1406288 (for **5**), 1406289 (for **16**), 1406290 (for **17**), 1406291 (for **21**), 1406292 (for **29**), 1406293 (for **35**), 1406294 (for **40**), 1406295 (for **42**), 1406296 (for **46**), and 1406297 (for **47**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The obtained crystal structures were analyzed for short contacts between non-bonded atoms using the PLATON program [25].

Fluoranil **4** was crystallized from CH_2Cl_2, 2-chloro-trifluoro-1,4-benzoquinone **32** and 2-methyl-trifluoro-1,4-benzoquinone **37** was crystallized from CCl_4. 2-Methoxy-trifluoro-1,4-benzoquinone **28** was prepared according to [17]. PPh_3 was crystallized from Et_2O. Aniline **15** and solvents were dried over CaH_2 and purified by high-vacuum distillation (0.09 kPa). 4-Phenoxyaniline **19** was crystallized from CH_2Cl_2-hexane (1:2).

*4.1.1. (4,5-Difluoro-2-oxido-3,6-dioxocyclohexa-1,4-dien-1-yl)triphenylphosphanium **5***

4.1.1.1. Method A

PPh_3 (0.728 g, 2.777 mmol) in C_6H_6 (3 mL) was added slowly to a stirred solution of fluoranil **4** (0.500 g, 2.777 mmol) in C_6H_6

(8 mL) at room temperature (Scheme 1). A green precipitate immediately separated. After 1 h the mixture was treated with water (3 mL), stirred for 4 h and was allowed to stand overnight. The mixture was centrifuged off from precipitate. A residue was treated with C_6H_6 (16 mL) and CH_2Cl_2 (20 mL), and was filtered from 0.675 g of insoluble material. The combined C_6H_6 and CH_2Cl_2 solutions afforded after double recrystallization betaine **5** (0.224 g, 19%) from C_6H_6 as bright yellow crystals. Crystals suitable for XRD analysis were grown from C_6H_6.

4.1.1.2. Method B

PPh_3 (0.437 g, 1.666 mmol) in dioxane (10 mL) was added slowly to a stirred solution of fluoranil **4** (0.300 g, 1.666 mmol) in dioxane (10 mL) and water (1 mL) at room temperature. After 48 h, a precipitate was centrifuged off, dried on air and after recrystallization betaine **22** was obtained from C_6H_6 as bright orange crystals (0.099 g, 9%). Dioxane solution was distilled off, the residue afforded after double recrystallization from C_6H_6 betaine **5** (0.171 g, 24%) as bright yellow crystals.

*4.1.2. Reaction between quinone **4** and PPh_3 in anhydrous C_6H_6 and fixing the formation of betaine **8***

PPh_3 (0.437 g, 1.666 mmol) in anhydrous C_6H_6 (3 mL) was added slowly to a stirred solution of fluoranil **4** (0.300 g, 1.666 mmol) in anhydrous C_6H_6 (5 mL) at room temperature under dried argon. A green precipitate immediately separated. After 30 min, the mixture was centrifuged off and the NMR spectra of green solution (0.329 g) were recorded under dried argon (see Scheme 1 see ESI[2] Supporting Chart 1). A green precipitate (0.408 g) was dissolved in Me_2SO and the NMR spectra of solution were recorded under dried argon with C_6F_6 (0.022 g, 0.118 mmol) as internal standard.

*4.1.3. [4-Fluoro-2-oxido-5-oxo-3-(phenylamino)-6-(phenylimino)cyclohexa-1,3-dien-1-yl]triphenylphosphanium **16***

PPh_3 (0.029 g, 0. 111 mmol) in anhydrous C_6H_6 (0.4 mL) was added slowly to a stirred solution of fluoranil **4** (0.020 g, 0. 111 mmol) in anhydrous C_6H_6 (0.4 mL) at room temperature under dried argon. A green precipitate immediately separated. After 1 h, the mixture was centrifuged off from precipitate. To benzene solution was slowly added 0.6 equivalent of aniline **15** (0.006 g, 0.067 mmol) in anhydrous C_6H_6 (0.5 mL) under dried argon. After 1 h, the NMR spectra of mixture were recorded under dried argon (Scheme 2). The solvent was distilled off, the residue was purified by TLC (Sorbfil, diethyl ether, R_f = 0.4–1.0, 1 time and then chloroform–hexane, 6:1, R_f = 0.5, 4 times) to yield betaine **16** (0.018 g, 29%) as red crystals. Crystals suitable for XRD analysis were grown from methylene chloride/diethyl ether/hexane (1:10:4).

*4.1.4. [4-Fluoro-2-oxido-3,6-dioxo-5-(phenylamino)cyclohexa-1,4-dien-1-yl]triphenyl-phosphanium **17***

PPh_3 (0.029 g, 0. 111 mmol) in anhydrous C_6H_6 (0.4 mL) was added slowly to a stirred solution of fluoranil **4** (0.020 g, 0. 111 mmol) in anhydrous C_6H_6 (0.4 mL) at room temperature under dried argon. A green precipitate immediately separated. After 1 h the mixture was centrifuged off from precipitate and the NMR spectra of solution were recorded under dried argon (Scheme 2). To benzene solution was quickly added 2.0 equivalent of aniline **15** (0.021 g, 0.222 mmol) in anhydrous C_6H_6 (0.6 mL) under dried argon. The resulting solution was stirred for 1 h and the NMR spectra were recorded under dried argon. The solvent was distilled off, the residue was purified by TLC (Sorbfil, CH_2Cl_2, R_f = 0.1, 1 time and then acetone–hexane, 1:2, R_f = 0.2, 2 times) to yield betaine **17** with admixture 50% **6**. After double recrystallization from methylene chloride/diethyl ether (1:8), betaine **17** was obtained as red oil (0.015 g, 27%). Crystals suitable for XRD analysis were grown from $CHCl_3$/hexane (1:20).

*4.1.5. Reactions of **4** with PPh_3 in anhydrous Et_2O, THF and dioxane*

PPh_3 (0.029 g, 0. 111 mmol) in anhydrous solvent (0.4–1.0 mL) was added slowly to a stirred solution of fluoranil **4** (0.020 g, 0. 111 mmol) in anhydrous solvent (1.0–2.0 mL) at room temperature under dried argon. A precipitate immediately separated. After 30 min the mixture was centrifuged off from precipitate and the NMR spectra of solution were recorded under dried argon. A precipitate was dissolved in Me_2SO and the NMR spectra of solution were recorded under dried argon with C_6F_6 as internal standard.

*4.1.6. {4-Fluoro-2-oxido-5-oxo-3-[(4-phenoxyphenyl)amino]-6-(phenylimino)cyclohexa-1,3-dien-1-yl}triphenylphosphanium **20** and {4-fluoro-2-oxido-3,6-dioxo-5-[(4-phenoxyphenyl)amino]cyclohexa-1,4-dien-1-yl}triphenylphosphanium **21***

PPh_3 (0.728 g, 2.777 mmol) in anhydrous dioxane (1.0 mL) was added slowly to a stirred solution of fluoranil **4** (0.500 g, 2.777 mmol) in anhydrous dioxane (2.0 mL) at room temperature in dry-box under dried argon. A brown precipitate immediately separated. After 1 h the mixture was centrifuged off from precipitate and the NMR spectra of solution were recorded under dried argon (Scheme 3). Aniline **15** (0.056 g, 0.600 mmol) in anhydrous dioxane (0.3 mL) was added slowly to dioxane solution under dried argon. The resulting solution was stirred for 1 h and then 4-phenoxyaniline **19** (0.500 g, 2.700 mmol) in anhydrous dioxane (5 mL) was quickly added. After 1 h the NMR spectra of solution were recorded under dried argon. The solvent was distilled off, the residue was separated by TLC (Sorbfil, ethyl acetate, R_f = 0.8–1.0, 1 time and then methylene chloride–hexane, 1:1, 1 time) to yield **21** (R_f = 0.4, with admixture 10% **6**) and betaine **20** (R_f = 0.9).

Betaine **20** was obtained as red oil (0.336 g, 18%).

Betaine **21** was obtained after reprecipitation fraction (R_f = 0.4) from chloroform/diethyl ether (1:4), as red oil (0.417 g, 26%). Red crystals suitable for XRD analysis were grown from acetone/hexane (1:3).

*4.1.7. [2,4-Dioxido-3,6-dioxo-5-(triphenylphosphaniumyl)cyclohexa-1,4-dien-1-yl]triphenylphosphanium **22***

4.1.7.1. Method A

PPh_3 (0.146 g, 0.555 mmol) in dioxane (1.0 mL) was added slowly to a stirred solution of fluoranil **4** (0.050 g, 0.277 mmol) in dioxane (1.0 mL) and H_2O (0.5 mL) at room temperature (Scheme 4). After 30 min the solution of PPh_3 (0.073 g, 0.277 mmol) in dioxane (1.0 mL) was added slowly and stirred for 24 h (Scheme 4). Water (3.0 mL) was added, a precipitate was centrifuged off, washed with water (2.0 mL), dried on air and purified by TLC (Whatman, chloroform, R_f = 0.1, 5 times and then acetone, R_f = 0.1, 5 times). After double TLC under the same conditions and recrystallization from $CHCl_3$/hexane (1:4) betaine **22** was obtained as a complex with one molecule of $CHCl_3$, bright orange crystals (0.098 g, 53%).

4.1.7.2. Method B

PPh_3 (0.078 g, 0.298 mmol) in dioxane (1.0 mL) was added slowly to a stirred solution of betaine **5** (0.050 g, 0.119 mmol) in

dioxane (2.0 mL) at room temperature. A mixture was stirred at room temperature for 10 d. Water (0.2 mL) was added and the mixture was stirred for another 48 h (Scheme 4). The mixture was extracted with chloroform. The solvent was distilled off, the residue was purified by TLC (Whatman, acetone, R_f = 0.1, 4 times). After double TLC under the same conditions betaine **22** was obtained as a complex with one molecule of $CHCl_3$, bright orange crystals (0.040 g, 51%).

*4.1.8. Reaction between **4** and Me_2SO*

A solution of quinone **4** (0.010 g, 0.056 mmol) in Me_2SO (0.5 mL) was prepared and then was keep at room temperature while periodically recording NMR spectra (Scheme 5).

*4.1.9. Triphenyl[2,4,6-trioxido-3,5-bis(triphenylphosphaniumyl)phenyl]phosphanium **25***

A mixture of fluoranil **4** (0.050 g, 0.277 mmol), PPh_3 (0.437 g, 1.666 mmol) and Me_2SO (5.0 mL) was stirred at room temperature under dried argon for 12 d. Water (0.4 mL) was added and the mixture was stirred for another 48 h (Scheme 5). Water (20.0 mL) was added, a precipitate was centrifuged off, washed with water (20.0 mL), dried on air and purified by TLC (Whatman, chloroform–hexane, 1:2, R_f = 0.8–1.0, 2 times and then diethyl ether, R_f = 0.1–0.2, 3 times). Betaine **25** was obtained as a complex with one molecule of $CHCl_3$, orange crystals (0.053 g, 21%).

*4.1.10. Reaction of **4** with PPh_3 in Me_2SO*

PPh_3 (0.029 g, 0.111 mmol) in Me_2SO (0.36 mL) was added slowly to a stirred solution of fluoranil **4** (0.020 g, 0.111 mmol) in Me_2SO (0.32 mL) at room temperature under dried argon and stirred for 1 h. Water (30.0 mL) was added, a precipitate was centrifuged off, washed with water (10.0 mL) and dried on air. The NMR spectra of precipitate were recorded in $CHCl_3$ (Scheme 5).

*4.1.11. Reaction between **4** and MeOH*

A solutions of quinone **4** with different concentrations (0.12–1.04 mol/l) in MeOH were prepared and then were keep at room temperature while periodically recording NMR spectra (Scheme 6).

*4.1.12. Reaction of **4** with PPh_3 in MeOH*

PPh_3 (0.029 g, 0.111 mmol) in MeOH (1.0 mL) was quickly added to a stirred solution of fluoranil **4** (0.020 g, 0.111 mmol) in MeOH (0.32 mL) at room temperature. After 1 h the NMR spectra of solution were recorded (Scheme 6).

*4.1.13. (4-Fluoro-5-methoxy-2-oxido-3,6-dioxocyclohexa-1,4-dien-1-yl)triphenylphosphanium **29***

PPh_3 (0.073 g, 0.278 mmol) in MeOH (3.2 mL) was quickly added to a stirred solution of fluoranil **4** (0.050 g, 0.278 mmol) in methanol (0.8 mL) at room temperature (Scheme 6). After 72 h, a precipitate was centrifuged off, dried on air and betaine **29** was obtained as bright orange crystals (0.059 g, 49%). Crystals suitable for XRD analysis were grown from $CHCl_3$.

*4.1.14. (5-Chloro-4-fluoro-2-oxido-3,6-dioxocyclohexa-1,4-dien-1-yl)triphenylphosphanium **35***

4.1.14.1. Method A

PPh_3 (0.400 g, 1.527 mmol) in anhydrous C_6H_6 (1.0 mL) was added slowly to a stirred solution of quinone **32** (0.300 g, 1.527 mmol) in anhydrous C_6H_6 (3.0 mL) at room temperature under dried argon. A brown precipitate immediately separated. After 30 min the mixture was centrifuged off from precipitate and the NMR spectra of solution were recorded under dried argon (Scheme 8). After 48 h the NMR spectra of solution were recorded over again under dried argon. The solvent was distilled off, a residue was purified by TLC (Sorbfil, chloroform, R_f = 0.3, 2 times) to yield betaine **35** as orange oil, (0.021 g, 3%).

A brown precipitate (0.228 g) was dissolved in Me_2SO and the NMR spectra of solution were recorded under dried argon with C_6F_6 (0.027 g, 0.145 mmol) as internal standard.

4.1.14.2. Method B

PPh_3 (0.667 g, 2.544 mmol) in anhydrous dioxane (1.0 mL) was added slowly to a stirred solution of quinone **32** (0.500 g, 2.544 mmol) in anhydrous dioxane (1.5 mL) at room temperature in dry-box under dried argon. A yellow precipitate immediately separated. After 1 h, the mixture was centrifuged off from precipitate and the NMR spectra of solution were recorded under dried argon (Scheme 8). After 96 h the NMR spectra of solution were recorded over again under dried argon. The solvent was distilled off, the residue was purified by TLC (Sorbfil, chloroform, R_f = 0.3, 2 times) to yield betaine **35** as orange oil, (1.240 g, 14%). Crystals suitable for XRD analysis were grown from acetone/hexane (1:5).

A yellow precipitate (0.163 g) was dissolved in Me_2SO and the NMR spectra of solution were recorded under dried argon with C_6F_6 (0.022 g, 0.118 mmol) as internal standard.

*4.1.15. (4-Fluoro-5-methyl-2-oxido-3,6-dioxocyclohexa-1,4-dien-1-yl)triphenylphosphanium **40** and [4-fluoro-3-hydroxy-5-methyl-2-oxido-6-oxo-3-(2-oxopropyl)cyclohexa-1,4-dien-1-yl]triphenylphosphanium **42***

PPh_3 (0.596 g, 2.271 mmol) in anhydrous dioxane (1.0 mL) was added slowly to a stirred solution of quinone **37** (0.400 g, 2.271 mmol) in anhydrous dioxane (1.5 mL) at room temperature in dry-box under dried argon. A black precipitate immediately separated. After 1 h, the mixture was centrifuged off from precipitate and the NMR spectra of solution were recorded under dried argon (Scheme 8). After 24 h the NMR spectra of solution were recorded over again under dried argon. The solvent was distilled off, the first part of the residue was purified by TLC (Sorbfil, acetone–hexane, 1:1, R_f = 0.5, 1 time) to yield a mixture of betaines **40** and **42** in (1:1) ratio. The mixture was separated by TLC (Sorbfil, ethyl acetate, 1 time) to yield:

Betaine **40** (R_f = 0.8, 0.087 g, 9%), orange oil. Orange crystals suitable for XRD analysis were grown from acetone/hexane (1:4).

Betaine **42** (R_f = 0.6, 0.099 g, 9%), yellow oil. Yellow crystals suitable for XRD analysis were grown from acetone/hexane (1:4).

The second part of the residue was purified by double TLC (Sorbfil, chloroform, R_f = 0.1, 1 time) to yield an additional amount of betaine **40** (0.047 g, 5%), an overall yield of **40** being (0.134 g, 14%).

A black precipitate (0.239 g) was dissolved in Me_2SO and the NMR spectra of solution were recorded under dried argon with C_6F_6 (0.028 g, 0.150 mmol) as internal standard.

*4.1.16. [4-Methoxy-2-oxido-5-oxo-3-(phenylamino)-6-(phenylimino)cyclohexa-1,3-dien-1-yl]triphenylphosphanium **46** and [4-methoxy-2-oxido-3,6-dioxo-5-(phenylamino)cyclohexa-1,4-dien-1-yl]triphenylphosphanium **47***

PPh_3 (0.375 g, 1.430 mmol) in anhydrous C_6H_6 (1.0 mL) was added slowly to a stirred solution of quinone **28** (0.275 g, 1.430 mmol) in anhydrous C_6H_6 (4.0 mL) at room temperature in dry-box under dried argon. A black precipitate immediately

separated. After 1 h, the mixture was centrifuged off from precipitate and the NMR spectra of solution were recorded under dried argon (Scheme 10). To benzene solution was quickly added 3.0 equivalent of aniline **15** (0.400 g, 4.290 mmol) in anhydrous C_6H_6 (1.0 mL) under dried argon. The resulting solution was stirred for 1 h and the NMR spectra were recorded under dried argon. The solvent was distilled off, the residue was separated by TLC (Sorbfil, $CHCl_3$, 3 times) to yield:

Betaine **46** (R_f = 0.4, 0.354 g, 43%), as red oil. Crystals suitable for XRD analysis were grown from $CHCl_3$/Et_2O/hexane (1:2:1).

Betaine **47** (R_f = 0.1, with admixture of 10% **6**). After double TLC (Sorbfil, acetone–hexane, 2:1, R_f = 0.4) betaine **47** was obtained as red oil, (0.052 g, 7%). Crystals suitable for XRD analysis were grown from acetone/hexane (1:3).

*4.1.17. [4-Methoxy-2-oxido-3,6-dioxo-5-(phenylamino)cyclohexa-1,4-dien-1-yl]triphenylphosphanium **47***

PPh_3 (0.683 g, 2.603 mmol) in anhydrous dioxane (1.0 mL) was added slowly to a stirred solution of quinone **28** (0.500 g, 2.603 mmol) in anhydrous dioxane (2.0 mL) at room temperature in dry-box under dried argon. A black precipitate immediately separated. After 1 h, the mixture was centrifuged off from precipitate and the NMR spectra of solution were recorded under dried argon (Scheme 9). After 24 h the NMR spectra of solution were recorded over again under dried argon. To dioxane solution was quickly added aniline **15** (0.102 g, 1.097 mmol) in chloroform (6.0 mL) and the resulting solution was stirred for 1 h. The solvent was distilled off, the residue was separated by TLC (Sorbfil, acetone–hexane, 2:1, R_f = 0.4). After double TLC under the same conditions betaine **47** was obtained as red oil, (0.073 g, 6%).

A black precipitate (0.211 g) was dissolved in Me_2SO and the NMR spectra of solution were recorded under dried argon with C_6F_6 (0.021 g, 0.113 mmol) as internal standard.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2015.08.018.

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