

Nucleophilic substitution in *O*-phenyldibenzofuranium and 10-phenylxanthonium cations

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Reactions of *O*-phenyldibenzofuranium tetrafluoroborate with nucleophiles (OH^- , NO_2^- , AcO^-) in aqueous media follow the $\text{S}_{\text{N}}\text{Ar}$ -mechanism and involve dehydroarenes. In DMSO, this salt smoothly reacts with NO_2^- and I^- with predominant opening of the furan ring. 10-Phenylxanthonium tetrafluoroborate readily arylates the NO_2^- ion in water (at the N and O atoms), mainly with predominant opening of the central ring, and is completely decomposed even with weak bases (NH_2OH , 2,4-dinitrophenylhydrazine). The Baeyer–Villiger oxidation of this salt affords xanthone and 2-phenoxybenzoic acid.

Key words: *O*-phenyldibenzofuranium salts, 10-phenylxanthonium salts, oxonium salts, nucleophilic substitution, dehydrobenzene, dehydroarenes, tribenzo[*b,d,f*]oxepine, Baeyer–Villiger reaction.

Unlike the Meerwein trialkyloxonium salts, triaryl-oxonium salts are known to be extremely inert toward low-basicity nucleophiles, while their ability to arylate bases is slightly higher.¹

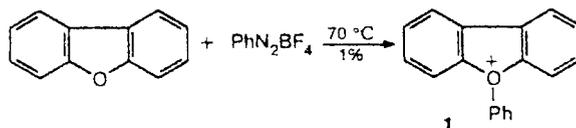
We assumed that these features of the behavior of triaryloxonium salts are due to purely steric reasons. As shown by Olah,² the Ph_3O^+ cation has a propeller-like geometry, and its α -carbon atoms are not easily accessible to nucleophilic attack. We have found recently that bases react with triaryloxonium according to another mechanism with intermediate formation of dehydroarenes³ (Scheme 1).

Using two cyclic oxonium salts, *O*-phenyldibenzofuranium tetrafluoroborate (**1**) and 10-phenylxanthonium tetrafluoroborate (**2**) as examples, in this work we tried to determine the influence of the cation geometry and ring size on the reactivity of the cation.

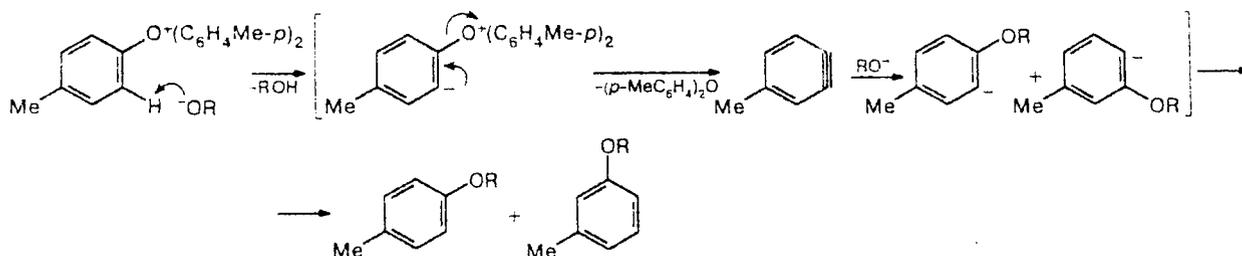
Results and Discussion

We synthesized salt **1** from 2-amino-2'-nitrobiphenyl by the known procedure⁴ and also by phenylation of dibenzofuran with phenyldiazonium tetrafluoroborate in a mixture of trifluoroacetic acid with hexafluorobenzene (Scheme 2), by analogy with the previously described synthesis of diarylchloronium salts.⁵

Scheme 2



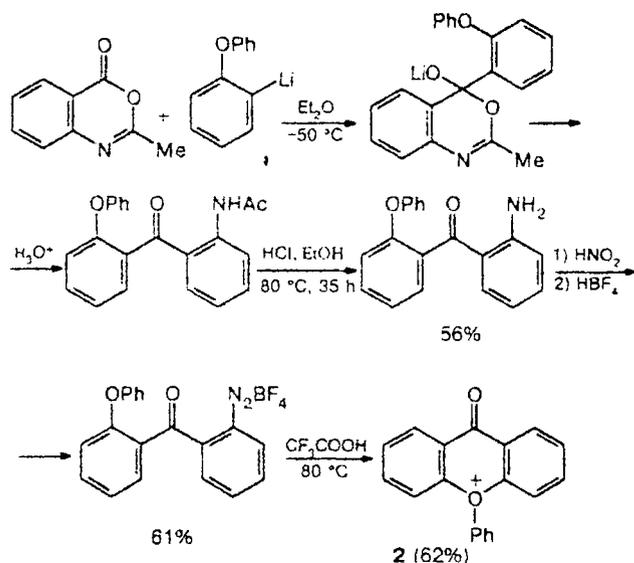
Scheme 1



The first method is more preferable, despite the many steps required, since the target product is formed in a significantly higher yield.

Salt **2** was synthesized according to Scheme 3.

Scheme 3



The structure of **2** was proved as follows. The exchange reaction with NaI afforded the corresponding iodide (**3**), the thermolysis of which yielded 2'-iodo-2-phenoxybenzophenone (with xanthone and iodobenzene as admixtures).

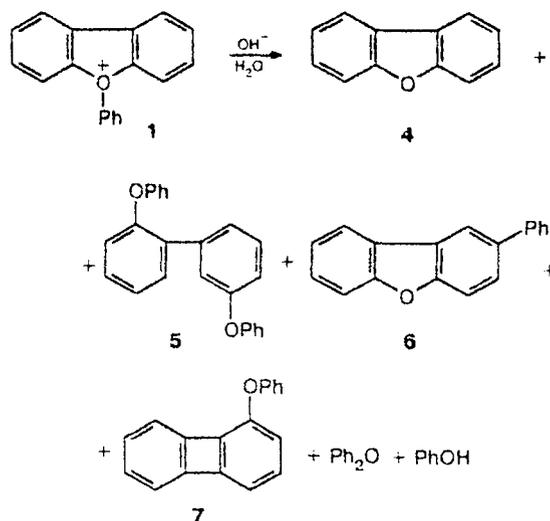
In turn, the structure of 2'-iodo-2-phenoxybenzophenone was proved by its independent synthesis from 2'-amino-2-phenoxybenzophenone and by its mass spectrum, which contained peaks of fragmentation ions with m/z 273 $[M-1]^+$ and 231 $[M-PhOC_6H_4]^+$, along with a molecular ion peak with m/z 400 (I_{rel} 51 %).

As in the case of triphenyloxonium, refluxing for many hours is needed for the completion of the reactions of salt **1** with the OH^- , NO_2^- , and AcO^- anions in aqueous medium. In spite of the fact that the dibenzofuran ligand is planar and the cation of salt **1** can no longer have a propeller-like geometry, steric hindrance for an S_N -reaction may still exist, especially since the nucleophiles are strongly solvated under these conditions.

The main products of the reaction of salt **1** with NaOH in water are phenol, dibenzofuran (**4**), and 2,3'-diphenoxybiphenyl (**5**) (in a 0.2 : 1 : 0.26 ratio), while the minor products are 2-phenyldibenzofuran (**6**) (~3 %), 1-phenoxybiphenylene (**7**) (~1 %), and traces of diphenyl oxide (Scheme 4).

This set of products, especially the presence of compound **5** among them, indicates that the reaction of salt **1** with the hydroxide ion involves the intermediate for-

Scheme 4



mation of dehydroarenes, as in similar reactions of triaryloxonium salts,³ and is complicated by further transformations of the primary products. The reaction proceeds in both possible directions, both with elimination of the phenyl group and with opening of the furan ring. The first, dominating direction involves an initial attack on the hydrogen atoms in *ortho*-positions of the phenyl group of **1** by the hydroxide ion. These atoms are more "acidic" and probably more sterically accessible than protons of the dibenzofuran moiety since, according to X-ray structural data,⁶ the benzene ring is turned by 76.9° relative to the dibenzofuran plane. This attack is accomplished by the formation of dibenzofuran and dehydrobenzene. The latter is transformed into the phenolate ion (and partially into diphenyl oxide) and probably may also electrophilically phenylate dibenzofuran at position 2 (Scheme 5), similarly to the phenylation of *N*-methylindole at position 3 by dehydrobenzene.⁷

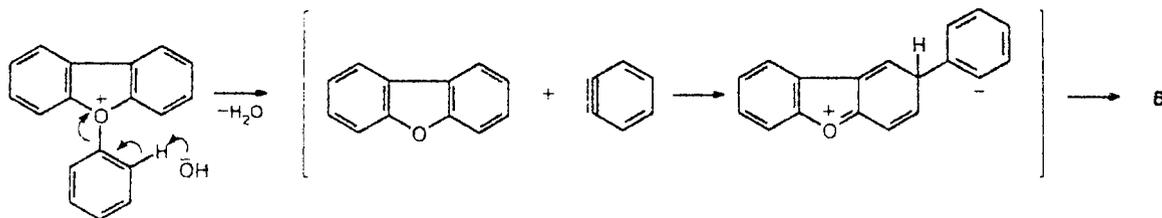
The second direction of the reaction that begins with an attack on the hydrogen atom in position 1 of the dibenzofuran fragment by a hydroxide ion is accomplished by the formation of 2,3-dehydro-2'-phenoxybiphenyl (dehydroarene A, Scheme 6). Its reaction with the phenolate ion gives 2,3'-diphenoxybiphenyl, since the rather bulky phenolate ion can attack only the less sterically hindered end of the triple bond of dehydroarene A.

Finally, 1-phenoxybiphenylene (**7**) is probably formed from dehydroarene A, too, by intramolecular cyclization.

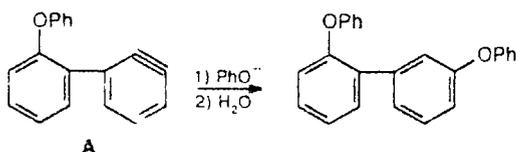
The reaction of salt **1** with NaOH in methanol to give anisole, compound **4**, 2'-methoxy-2-phenoxy- and 3'-methoxy-2-phenoxybiphenyls (**8** and **9**) (in a 1 : 1 : 0.01 : 0.4 ratio) occurs noticeably faster (Scheme 7).

As could be expected, under these conditions the effect of steric factors on both the ratio of the two reaction directions and the ratio of isomers **8** and **9**

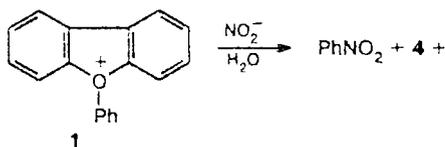
Scheme 5



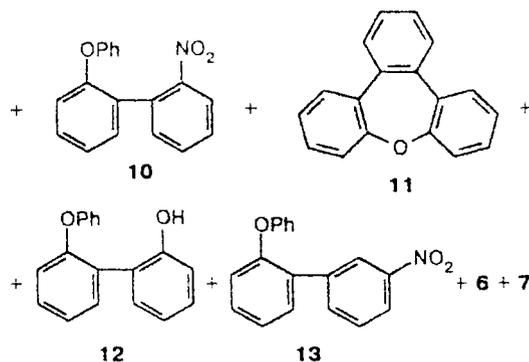
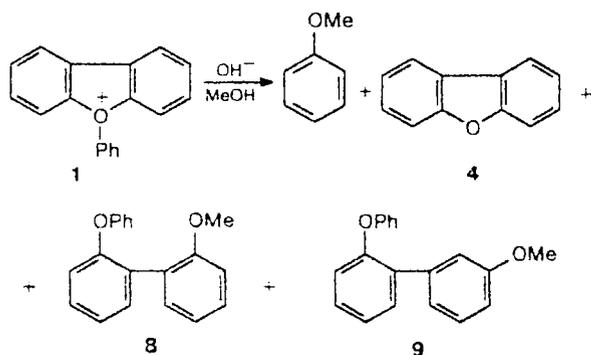
Scheme 6



Scheme 8



Scheme 7



manifests itself even more clearly due to the increase in the bulk of the reagents.

The reaction of salt **1** with NaNO_2 in water also affords a multi-component mixture of products. The evolution of nitrogen oxides is observed in the course of the reaction. The major products are nitrobenzene, compound **4**, 2'-nitro-2-phenoxybiphenyl (**10**), and tribenzo[*b,d,f*]oxepine (**11**) (in a 0.34 : 1 : 0.85 : 0.47 ratio) (Scheme 8).

In addition, very small amounts (1–2%) of compounds **6**, **7**, 2'-hydroxy-2-phenoxybiphenyl (**12**), and 3'-nitro-2-phenoxybiphenyl (**13**) are formed.

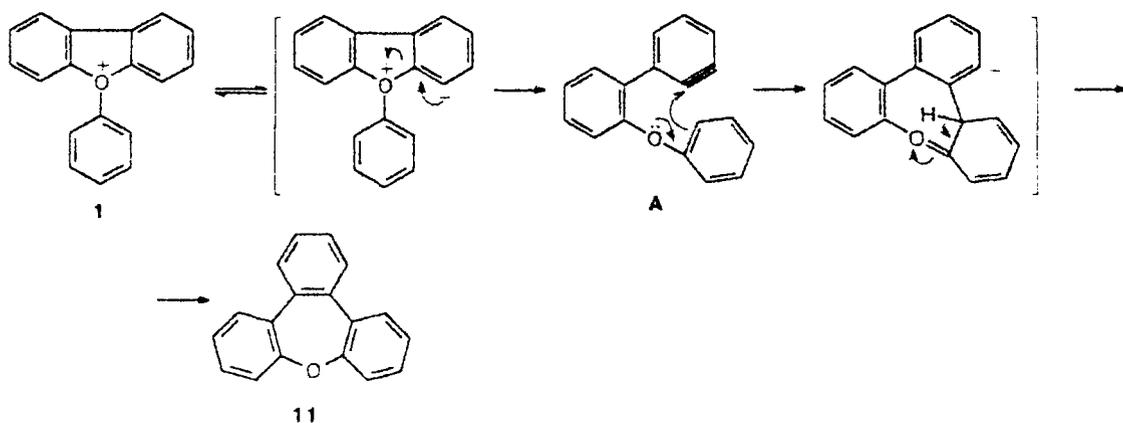
It is clear that the direction of the reaction with opening of the furan ring prevails in this case. The arylation of the NO_2^- ion with the cation of salt **1** probably occurs by the $\text{S}_{\text{N}}\text{Ar}$ mechanism (an attack on the α -C atom) and affords mainly the *N*-arylation product, compound **10**. In parallel, *O*-arylation of the nitrite ion producing compound **12** and nitrogen oxides (hydrolysis of the corresponding aryl nitrite) is observed. However, the most interesting and unexpected result of

the reaction is undoubtedly the formation of tribenzo[*b,d,f*]oxepine.

This compound was obtained for the first time by thermolysis of 2-chlorosulfonyl-2'-phenyldiphenyl oxide at 250–260 °C and also upon copper-induced decomposition of diazotized 2-amino-2'-phenyldiphenyl oxide,⁸ *i.e.*, in the reactions involving a radical mechanism. However, it is unlikely that triaryloxonium salts are capable of radical decomposition, since they do not react with metals⁹ and since products of radical origin, such as arenes or diaryls, have never been observed in any of their reactions. Therefore, a radical path of the formation of **11** from salt **1** should be ruled out. We also found that nitro compound **10** is not transformed into **11** under the reaction conditions. The formation of the latter from phenol **12** under these mild conditions (water, 100 °C) is also improbable. However, this pathway cannot be totally ruled out, since phenol **12** is still present among the minor reaction products.

In our opinion, the most probable pathway for the synthesis of tribenzo[*b,d,f*]oxepine **11** is as follows. It is known that NaNO_2 can undergo hydrolysis in aqueous solutions (in our case, $\text{pH} = 8.6$), and therefore hydrox-

Scheme 9



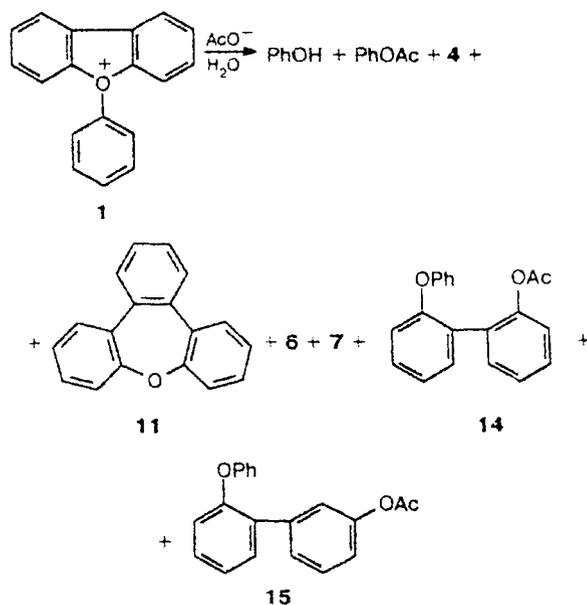
ide ion* rather than nitrite ion can be the reagent responsible for the formation of **11**. Initially, the hydroxide ion reversibly detaches a proton from the *ortho*-position of a phenyl or a dibenzofuran moiety to generate the corresponding dehydroarenes. Dehydrobenzene can add an NO_2^- ion with subsequent transformation into nitrobenzene, and the dehydroarene fragment of intermediate **A** (Scheme 9) attacks the *ortho*-position of the adjacent phenyl group by the electrophilic mechanism. Intramolecular cyclization finally affords the thermodynamically stable¹¹ tribenzo[*b,d,f*]oxepine **11**.

This thermodynamically controlled reaction path probably becomes possible only at low concentrations of the OH^- ion. With a large excess of this ion, this direction is not realized, as we have observed in the reaction of salt **1** with NaOH . The intermediate formation of both dehydroarenes is also confirmed by the presence of compounds **6**, **7**, and especially **13** among the minor reaction products.

To check our hypothesis regarding the pathway of the synthesis of tribenzo[*b,d,f*]oxepine, we carried out the reaction of salt **1** with an aqueous solution of NaOAc (pH 9.3). It turned out that this reaction also follows two possible directions (Scheme 10). As in the reaction with the OH^- ion, the elimination of the phenyl group and the intermediate formation of both dehydroarenes are mainly observed. Dehydrobenzene is subsequently transformed into phenol and partially into phenyl acetate, while dehydroarene **A**, as we expected, gives tribenzo[*b,d,f*]oxepine **11** (**11** : **4** = 0.22 : 1) (Scheme 10).

Compounds **6**, **7**, and isomeric 2'-acetoxy- and 3'-acetoxy-2-phenoxybiphenyls (**14** and **15**) were also found among the minor reaction products. The presence of these compounds in the reaction mixture confirms that the reaction involves the formation of dehydroarenes.

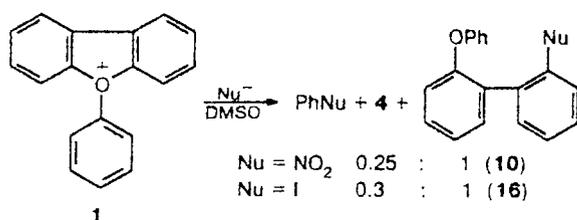
Scheme 10



The reaction of salt **1** with NaNO_2 was also carried out in DMSO. It was completed in 5 h and, as could be expected, occurred smoothly, mainly through the furan ring opening, and was not complicated with any side processes (Scheme 11). Only dibenzofuran, nitrobenzene, and nitro compound **10** were found in the reaction mixture. The reaction of salt **1** with NaI in DMSO occurred in exactly the same way and afforded the iodobenzene and 2'-iodo-2-phenoxybiphenyl (**16**), correspondingly. Both compounds **10** and **16** are probably formed by an $\text{S}_{\text{N}}\text{Ar}$ -type mechanism through direct attack of the nucleophile at the less sterically hindered C(1) atom of the dibenzofuran moiety of salt **1**.

*Side reactions involving the OH^- ion were observed by us earlier in the reaction of the 10*H*-dibenzo[*b,e*]iodinium cation with NaNO_2 in water.¹⁰

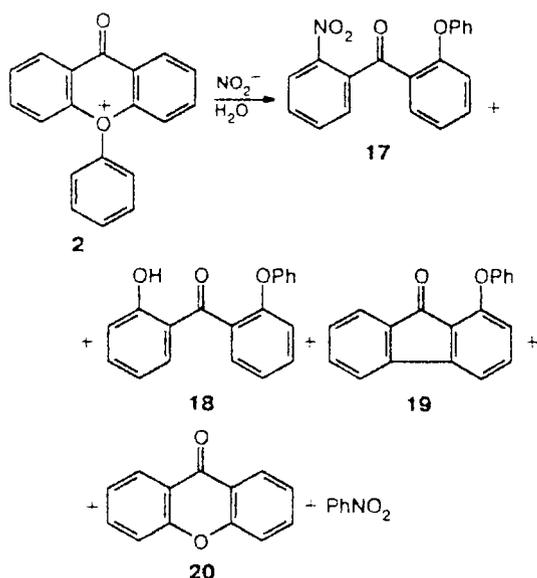
Scheme 11



Thus, reactions of cation **1** with low-basicity nucleophiles (probably, by the S_NAr type mechanism) primarily result in the furan ring opening. If the nucleophile is a strong base, the intermediates mainly include dehydroarenes, mostly dehydrobenzene, due to the fact that initial attack of the reagent at the more sterically accessible H atoms in *ortho*-positions of the phenyl radicals predominates.

10-Phenylxanthonium tetrafluoroborate (**2**) reacts with nucleophiles in a totally different way. For example, unlike salt **1** and triphenyloxonium salts,¹ it is completely decomposed on boiling with an aqueous solution of NaNO_2 already in 3 h in the two possible directions with the predominant opening of the heterocycle (Scheme 12).

Scheme 12



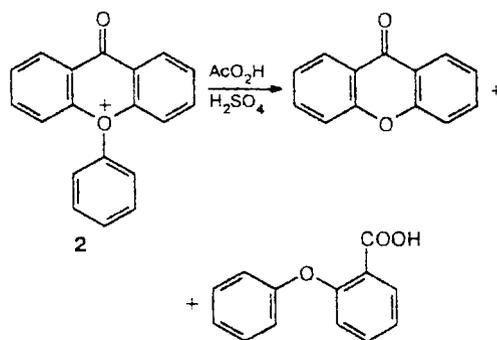
The main product of this reaction pathway, 2'-nitro-2-phenoxybenzophenone (**17**), is formed as a result of *N*-arylation of the NO_2^- ion with the cation of salt **2**. 2'-Hydroxy-2-phenoxybenzophenone (**18**), which can be formed due to both the *O*-arylation of the nitrite ion and hydrolysis of cation **2** (see below), is also present but in a noticeably smaller amount. Finally, 1-phenoxy-

fluorenone (**19**), one more product of this reaction pathway, may be formed from **18**. The second reaction pathway affords nitrobenzene and xanthone (**20**).

Two reaction centers, the oxonium group and the carbonyl group, are present in the cation of salt **2**. However, the first one appeared to be incomparably more reactive. We were not able to carry out reactions at the carbonyl group of **2** without affecting the onium center. For example, salt **2** is readily decomposed under the action of reagents typically used for the determination of the carbonyl group, such as hydroxylamine (and its hydrochloride) or 2,4-dinitrophenylhydrazine (in the presence of HBF_4). It should be noted that the latter reagent does form the corresponding derivative of a similar iodonium salt, 10-oxodibenzo[*b,e*]iodinium tetrafluoroborate, in ~90% yield, despite the fact that in other reactions the onium center of this cation is also more reactive than the carbonyl group.¹²

We were also unable to carry out Baeyer–Villiger oxidation of salt **2** with retention of the onium system. In this case, the onium center also appeared to be more reactive than the carbonyl group. Peroxysulfuric acid ($\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$) completely decomposes salt **2** in one day. Peracetic acid in the presence of concentrated H_2SO_4 at 20 °C reacts with salt **2** very slowly: iodide **3** was isolated from the reaction mixture after treatment with NaI in a quantitative yield after 4 days. Prolonged (16 days) action of peracetic acid on salt **2** in the presence of excess H_2SO_4 at 20 °C affords xanthone (40%) and 2-phenoxybenzoic acid (58%) (Scheme 13).

Scheme 13



The formation of xanthone indicates that peracetic acid directly attacks the carbon atoms bound to the oxonium oxygen. The second possible reaction product, 2'-hydroxy-2-phenoxybenzophenone (**18**) (or its ester with peracetic acid), subsequently gives normal products of the Baeyer–Villiger oxidation, 2-phenoxybenzoic acid and pyrocatechol. The latter product, as well as phenol formed along with xanthone, undergo further transformations under the reaction conditions; therefore, they could not be isolated and identified.

Table 1. Temperatures of decomposition of oxonium salts, °C

Anion	Cation		
	2	1	Ph ₃ O ⁺
BF ₄ ⁻	133–134	175–176	226 ¹
I ⁻	113–114	137–138 ⁴	177–178 ¹

Substantially lower decomposition temperatures of the salts of cation **2** (Table 1) also indicate its lower stability as compared with cation **1** and Ph₃O⁺.

Thus, the reactivity of salt **2** completely differs from those of both non-cyclic triphenyloxonium and salt **1**, whose onium center is incorporated into the five-membered ring. One of the reasons for this behavior of salt **2** is probably the activation of the onium center by the carbonyl group. However, the data obtained by a comparative analysis of ¹³C NMR spectra of triphenyloxonium tetrafluoroborate (**22**) and 10-phenylxanthonium tetrafluoroborate, as well as their neutral analogs, diphenyl oxide (**23**) and 2-phenoxybenzophenone (**21**), do not confirm this assumption (Table 2). The signals of almost all the C atoms of both cations are noticeably shifted downfield as compared with their neutral analogs, while the chemical shifts of the C(1') atoms in the 10-phenylxanthonium cation and of the C(1) atoms in the triphenyloxonium cation are practically the same. The differences in the chemical behavior of the triphenyloxonium and 10-phenylxanthonium salts probably result from the steric rather than the electronic factors, since the differences in the chemical shifts of the C(1') and C(1) atoms of compounds **2** and **21**, on the one hand, and those of the C(1) atoms of compounds **22** and **23**, on the other hand, are very close (see Table 2).

Unlike the triphenyloxonium cation ("symmetrical propeller") and the *O*-phenyldibenzofuranium cation, whose onium atom is fixed in a rigid five-membered ring, the 10-phenylxanthonium cation with a more flexible six-membered ring can adopt in solution a conformation in which the oxonium atom is at the top of a pyramid and the C atoms linked with the oxonium atom are in its base. In this case the steric hindrances around the onium center are noticeably decreased, and cation **2** can easily react both with nucleophiles and bases, even with the weak ones.

It should be noted that 10-oxodibenzo[*b,e*]iodinium¹³ and *S*-phenylphenoxathiinium¹⁴ cations with similar structures are not planar even in the crystalline state (X-ray structural data). The central ring in these cations is bent around the I⁺—C (or S⁺—O) line and the sulfonium atom has a pyramidal configuration.

All of the reaction products discussed in this paper were characterized by their mass spectra. Phenol, anisole, diphenyl oxide, dibenzofuran, nitrobenzene, phenyl acetate, iodobenzene, and xanthone were identified by mass spectra using the data bank of the USA National Institute of Standards (NIST). The structures of other compounds are in agreement with the characteristic fragmentation of their molecular ions (Table 3).

Experimental

Chromato-mass spectral analysis was carried out on Kratos-MS-25-RFA (25 m × 0.32 mm capillary column with CP-SIL 8CB as the liquid phase and helium as the carrier gas, ionizing voltage 50 eV, source temperature 250 °C; the temperature was programmed as 170–250 °C, 4 deg min⁻¹), LKB-2091 (4 m × 0.32 mm capillary column with SE-54 as the liquid phase and helium as the carrier gas, rate 1.6 mL min⁻¹ at 70 °C, ionizing voltage 70 eV, source temperature 200 °C;

Table 2. Chemical shifts of ¹³C atoms in compounds **2** and **21–23**

Compound	δ*									
	C(1)	C(2)	C(3)	C(4)	C(1')	C(2')	C(3')	C(4')	C(5')	C(6')
2	159.8	134.5	123.6	138.7	162.4	124.0	131.8	130.5	138.7	118.9
21	156.6	117.8	128.3	122.1	158.2	127.1	130.3	121.8	132.4	117.5
Δδ	3.2	16.7	-5.1	16.6	4.2	-2.9	1.5	8.7	6.3	0.6
22	161.5	133.3	121.3	132.5						
23	156.6	117.8	128.3	122.1						
Δδ	4.9	15.5	-7.4	10.4						

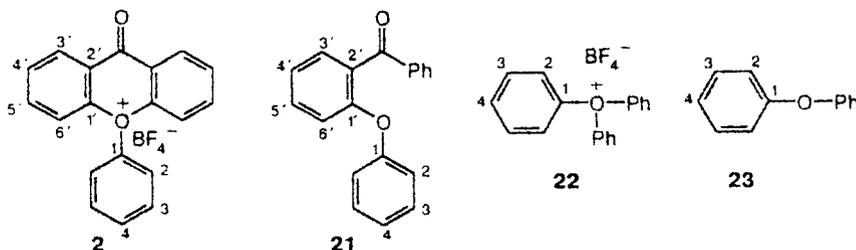
*Bruker WP-200 SY, acetone-d₆.

Table 3. Mass spectral data for compounds 3, 5–19

Compound	m/z (I_{rel} (%)), assignment							
3	400 (52) [M] ⁺	273 (100) [M-I] ⁺	231 (16) [M-PhOC ₆ H ₄] ⁺	204 (30) [Ph] ⁺	196 (79) [Xanthone] ⁺	168 (21) [196-CO] ⁺	139 (22) [168-HCO] ⁺	77 (52) [Ph] ⁺
5	338 (100) [M] ⁺	245 (19) [M-PhO] ⁺	168 (15) [245-Ph] ⁺	139 (12) [168-HCO] ⁺	77 (11) [Ph] ⁺			
6	244 (94) [M] ⁺	216 (56) [M-CO] ⁺	215 (100) [M-HCO] ⁺	189 (18) [215-C ₂ H ₂] ⁺	163 (5) [189-C ₂ H ₂] ⁺	77 (1) [Ph] ⁺		
7	244 (11) [M] ⁺	218 (100) [M-C ₂ H ₂] ⁺	189 (18) [218-HCO] ⁺	163 (6) [189-C ₂ H ₂] ⁺				
8	276 (100) [M] ⁺	245 (5) [M-MeO] ⁺	215 (13) [245-H-HCO] ⁺	183 (12) [M-PhO] ⁺	168 (92) [245-Ph] ⁺	152 (12) [183-MeO] ⁺	139 (41) [168-HCO] ⁺	91 (45)* [C ₇ H ₇] ⁺
9	276 (100) [M] ⁺	261 (12) [M-Me] ⁺	245 (8) [M-MeO] ⁺	215 (20) [245-H-HCO] ⁺	215 (20) [245-Ph] ⁺ or [261-PhO] ⁺	168 (12) [245-PhO] ⁺	152 (10) [168-HCO] ⁺	139 (29) [168-HCO] ⁺
10	291 (45) [M] ⁺	198 (100) [M-PhO] ⁺	168 (65) [198-NO] ⁺	139 (63) [168-HCO] ⁺	77 (38) [Ph] ⁺			
11	244 (100) [M] ⁺	243 (6) [M-H] ⁺	242 (29) [M-2 H] ⁺	215 (22) [M-HCO] ⁺	213 (12) [242-HCO] ⁺	189 (9) [215-C ₂ H ₂] ⁺	163 (3) [189-C ₂ H ₂] ⁺	77 (0) [Ph] ⁺
12	262 (61) [M] ⁺	169 (100) [M-PhO] ⁺	168 (88) [169-H] ⁺	139 (34) [168-HCO] ⁺	77 (25) [Ph] ⁺			
13	291 (100) [M] ⁺	245 (30) [M-NO ₂] ⁺	219 (23) [245-C ₂ H ₂] ⁺	214 (32) [M-Ph] ⁺	168 (30) [245-NO ₂] ⁺	152 (16) [245-PhO] ⁺	139 (40) [168-HCO] ⁺	77 (42) [Ph] ⁺
14	304 (19) [M] ⁺	262 (84) [M-CH ₂ =CO] ⁺	233 (2) [262-CHO] ⁺	169 (100) [262-PhO] ⁺	168 (98) [169-H] ⁺	139 (29) [168-CHO] ⁺		
15	304 (23) [M] ⁺	262 (100) [M-CH ₂ =CO] ⁺	245 (9) [262-OH] ⁺	233 (6.5) [262-HCO] ⁺	168 (3) [M-Ph-AcO] ⁺	139 (14.5) [168-HCO] ⁺		
16	372 (100) [M] ⁺	279 (3) [M-PhO] ⁺	245 (72) [M-I] ⁺	227 (72) [279-2 C ₂ H ₂] ⁺	203 (30) [M-C ₆ H ₄ OPh] ⁺	168 (40) [M-I-Ph] ⁺	152 (46) [245-OPh] ⁺	139 (47)* [168-HCO] ⁺
17	319 (62) [M] ⁺	289 (14) [M-NO] ⁺	273 (23) [M-NO ₂] ⁺	272 (44) [289-OH] ⁺	197 (100) [M-C ₆ H ₄ NO ₂] ⁺	242 (4) [M-Ph] ⁺	213 (5) [242-HCO] ⁺	185 (63) [213-CO] ⁺
		157 (12) [185-CO] ⁺	141 (13) [157-O] ⁺	139 (16) [185-NO ₂] ⁺	115 (20) [141-CN] ⁺	77 (27) [Ph] ⁺		
18	290 (16) [M] ⁺	197 (100) [M-PhO] ⁺	196 (42) [197-H] ⁺	168 (20) [196-CO] ⁺	139 (14) [168-HCO] ⁺	121 (14) [M-C ₆ H ₄ OPh] ⁺	94 (16) [PhOH] ⁺	77 (10) [Ph] ⁺
19	272 (100) [M] ⁺	244 (8) [M-CO] ⁺	215 (14) [244-HCO] ⁺					

*In addition, the peak of the [Ph]⁺ ion with $m/z = 77$ is observed.

the temperature was programmed as 70–280 °C, 16 deg min⁻¹), and Finnigan MAT 112 S instruments (60 m×0.32 mm capillary column with DB-1 as the liquid phase and helium as the carrier gas, the temperature program was 40 (5 min)–260 °C, 12 deg min⁻¹). IR spectra were recorded on a UR-20 spectrophotometer (suspensions in Vaseline oil).

O-Phenyldibenzofuranium tetrafluoroborate (1). A solution of PhN₃⁺BF₄⁻ (20 g, 100 mmol) in CF₃COOH (50 mL) was added dropwise to a solution of dibenzofuran (8 g, 48 mmol) in a mixture of CF₃COOH (15 mL) and C₆F₆ (15 mL) at 70–80 °C, and the mixture was refluxed until a test with β-naphthol was negative. The solvents were removed, and the residue was treated with ether. Salt 1 that precipitated was reprecipitated with ether from acetone (after decolorization with activated carbon) and then from MeNO₂ to give 0.16 g (1%) of salt 1, m.p. 175–176 °C (cf., Ref. 4: m.p. 174–175 °C).

2'-Amino-2-phenoxybenzophenone. A solution of 2-lithiodiphenyl oxide prepared from a 1.23 M solution of *n*-butyl lithium in *n*-hexane (0.126 mol, 102.6 mL) and a solution of diphenyl oxide (21.28 g, 0.126 mol) in dry ether (63 mL)¹⁵ was added dropwise to a suspension of

2-methylbenzo-1,3-oxazine-4-one ("acetylanthranyl")* (20.36 g, 0.126 mol) in dry ether (450 mL) over 3 h with stirring under argon at -50 °C. The process was accompanied by the formation of a bright yellow precipitate. The mixture was allowed to stand for 1 day.

18% HCl (200 mL) was slowly added to the reaction mixture at 0 °C until the yellow precipitate dissolved completely. The aqueous layer was extracted with ether, and the extract was concentrated *in vacuo*. The residue was refluxed for 35 h in a mixture of concentrated HCl (300 mL) and ethanol (200 mL). Ethanol was distilled off, the residue was alkalized, and the target product was extracted with benzene. The solvent was distilled off, and the residue was distilled *in vacuo* to yield 20.24 g (56%) of 2'-amino-2-phenoxybenzophenone, b.p. 195–198 °C (1.5–1.1 · 10⁻² Torr), m.p. 112–113 °C (from EtOH). Found (%): C, 78.63; H, 5.15; N, 5.30. C₁₉H₁₅NO₂. Calculated (%): C, 78.87; H, 5.23; N, 4.84.

2-(2-Phenoxybenzoyl)phenyldiazonium tetrafluoroborate. 50% H₂SO₄ (26 mL) was added to a solution of 2'-amino-2-

*Prepared by the known procedure,¹⁶ b.p. 143 °C (11 Torr), m.p. 79–80 °C.

phenoxybenzophenone (11.83 g, 41 mmol) in a minimum amount of AcOH. The amine salt was diazotized with a concentrated aqueous solution of NaNO_2 (4.72 g, 68 mmol) at 0–5°C. Excess 40% HBF_4 was added to the transparent solution. The salt that precipitated was washed with ether. The aqueous filtrate was shaken with a $\text{MeNO}_2\text{--CHCl}_3$ mixture (3:1 v/v); the solvents were removed *in vacuo* and the residue was treated with ether to give an additional amount of the salt. The overall yield of 2-(2-phenoxybenzoyl)phenyldiazonium tetrafluoroborate was 9.77 g (61%).

10-Phenylxanthonium tetrafluoroborate (2). A solution of the diazonium salt (see above) (2.27 g, 5.85 mmol) in CF_3COOH (20 mL) was refluxed until complete decomposition of the diazonium salt (test with β -naphthole). The solvent was concentrated *in vacuo* to a minimum volume, and ether was added to precipitate 1.32 g (62%) of salt 2. The salt was purified by boiling in acetone with zinc dust followed by precipitation with ether from MeNO_2 . M.p. 133–134°C. Found (%): C, 63.08; H, 3.64; B, 3.10; F, 21.10. $\text{C}_{19}\text{H}_{13}\text{BF}_4\text{O}_2$. Calculated (%): C, 63.37; H, 3.64; B, 3.00; F, 21.11. IR, ν/cm^{-1} : 1680 (νCO); 1615, 1575 (νAr); 1050–1200 (BF_4).

10-Phenylxanthonium iodide (3). A concentrated solution of NaI in acetone was added to a solution of salt 2 (0.05 g, 0.14 mmol) in a minimum amount of acetone until precipitation was completed. The lemon-yellow precipitate was washed with water, ethanol, and ether and dried *in vacuo* to give 0.03 g (54%) of salt 3, m.p. 113.5–114°C. Found (%): C, 57.23; H, 3.39; I, 31.43. $\text{C}_{19}\text{H}_{13}\text{IO}_2$. Calculated (%): C, 57.02; H, 3.27; I, 31.71.

Reactions of *O*-phenyldibenzofuranium tetrafluoroborate (1).

a. With NaOH in water. A solution of salt 1 (100.6 mg, 0.3 mmol) and NaOH (120 mg, 3 mmol) in water (10 mL) was refluxed for 20 h until complete decomposition of the oxonium salt. The reaction mixture was acidified and extracted with ether (3×15 mL), and the extract was washed with water and dried with MgSO_4 . According to GLC/MS data, the extract contained phenol, dibenzofuran (4) and 2,3'-diphenoxybiphenyl (5) in a 0.2:1:0.26 ratio, and also very small amounts (1–3%) of 2-phenyldibenzofuran (6), 1-phenoxybiphenylene (7), and traces of Ph_2O .

b. With NaOH in methanol. A solution of 1 (100.5 mg, 0.3 mmol) and 6.25 M NaOH (0.48 mL, 3 mmol) in MeOH (5 mL) was refluxed for 10 h, diluted with water, extracted with ether (3×15 mL), and processed as described in *a*. According to GLC/MS data, the extract contained anisole, 4, 2'-methoxy-2-phenoxybiphenyl (8), and 3'-methoxy-2-phenoxybiphenyl (9) in a 1:1:0.01:0.4 ratio.

c. With NaNO_2 in water. A solution of 1 (333 mg, 1 mmol) and NaNO_2 (690 mg, 10 mmol) in water (15 mL) was refluxed for 30 h until complete decomposition of the oxonium salt. The reaction mixture was extracted with ether (3×15 mL), and the extract was washed with water and dried with CaCl_2 . According to GLC/MS data, the extract contained nitrobenzene, 4, 2'-nitro-2-phenoxybiphenyl (10), and tribenzo[*b,d,f*]oxepine (11) in a 0.34:1:0.85:0.47 ratio, and also 6, 7, 2'-hydroxy-2-phenoxybiphenyl (12) and 3'-nitro-2-phenoxybiphenyl (13) (~1% of each).

d. With AcONa in water. A solution of 1 (50.3 mg, 0.15 mmol) and AcONa (123 mg, 1.5 mmol) in water (10 mL) was refluxed for 30 h and then processed as in the previous run. According to GLC/MS data, the extract contained phenol, traces of phenyl acetate, 4, and tribenzo[*b,d,f*]oxepine (11), and also 2'-acetoxy-2-phenoxybiphenyl (14), 3'-acetoxy-2-phenoxybiphenyl (15) (~1% of each), and compounds 6 and 7.

e. With NaNO_2 in DMSO. A solution of 1 (100.6 mg, 0.3 mmol) and NaNO_2 (207 mg, 3 mmol) in DMSO was heated at 90–100°C until complete decomposition of the oxonium salt (5 h). The reaction mixture was diluted with water (10 mL) and extracted with ether (3×15 mL). The ethereal extract was thoroughly washed with water and dried with CaCl_2 . According to GLC/MS data, the extract contained two main products, 4 and 2'-nitro-2-phenoxybiphenyl (10), in a 0.25:1 ratio. It was impossible to extract PhNO_2 and PhI formed (10–12 mg) from the solution in aqueous DMSO with ether. Their formation was recorded by TLC.

f. With NaI in DMSO. A solution of 1 (100.5 mg, 0.3 mmol) and NaI (450 mg, 3 mmol) in DMSO (4 mL) was heated at 90–100°C until complete decomposition of the oxonium salt (5 h) and then processed as in *e*. According to GLC/MS data, the ethereal extract contained 4 and 2'-iodo-2-phenoxybiphenyl (16) in a 0.3:1 ratio.

Reactions of 10-phenylxanthonium tetrafluoroborate (2).

a. With NaNO_2 in water. A solution of salt 2 (0.11 g, 0.3 mmol) and NaNO_2 (0.21 g, 3 mmol) in water (5 mL) was refluxed until complete decomposition of the oxonium salt (3 h). The reaction mixture was cooled and extracted with CHCl_3 , and the extract was washed with water and dried with MgSO_4 . According to GLC/MS data, the extract contained nitrobenzene (2%), xanthone (20) (15%), 2'-hydroxy-2-phenoxybenzophenone (18) (12%), 1-phenoxyfluorenone (19) (12%), and 2'-nitro-2-phenoxybenzophenone (17) (57%).

b. With 2,4-dinitrophenylhydrazine. A solution of compound 2 (0.1 g, 0.28 mmol) in EtOH (20 mL) was added to a hot solution of 2,4-dinitrophenylhydrazine (0.4 g, 2 mmol) in a mixture of 40% HBF_4 (10 mL) and EtOH (10 mL). The mixture was refluxed for 30 min. Ethanol was distilled *in vacuo*, and the residue was treated with excess ether. In this case, no salt-like products were found.

c. With peracetic acid in acetic acid. A 28% solution of AcO_2H (0.3 mL) was added dropwise with stirring at 0–5°C to a solution of salt 2 (0.18 g, 0.5 mmol) in a mixture of AcOH (3 mL) and concentrated H_2SO_4 (0.76 mL). The mixture was kept at 20°C for 98 h and then diluted 10-fold with water. The solution was treated with Na_2SO_3 and then with excess NaI. The precipitate of 10-phenylxanthonium iodide (3) was washed with water, ethanol, and ether and dried. The yield of 3 was 0.19 g (95%), m.p. 113.5–114°C after reprecipitation from MeNO_2 with ether. A mixture with an authentic sample did not show depression of the melting point.

d. With peracetic acid in concentrated H_2SO_4 . A solution of salt 2 (0.73 g, 2 mmol) in concentrated H_2SO_4 (2.5 mL) was mixed with 25% peracetic acid (3 mL) at 0–5°C, and the mixture was kept at 20°C for 16 days. The mixture was then poured onto ice and carefully treated with 20% NaOH until the medium was alkaline, and the product was extracted with benzene. The benzene was distilled off to give 0.17 g (43%) of xanthone in the residue, which was crystallized from ethanol and sublimed *in vacuo*, m.p. 173–174°C (*cf.*, Ref. 17; m.p. 174–176°C). IR, ν/cm^{-1} : 1670 (νCO); 1610, 1585 (νAr) (*cf.*, Ref. 18). The alkaline solution that remained after isolation of xanthone was acidified and extracted with chloroform to yield 0.25 g (58%) of 2-phenoxybenzoic acid, m.p. 110–112°C (*cf.*, Ref. 19; m.p. 113°C). IR, ν/cm^{-1} : 1680 (νCO); 3200–2600 (νOH).

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