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Phenyliodoniophenolates from 1,3-Dihydroxybenzene Derivatives

Spyros Spyroudis* and Petroula Tarantili

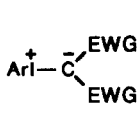
Laboratory of Organic Chemistry, Chemistry Department, University of Thessaloniki, Thessaloniki 54006, Greece.

Abstract: A new type of phenyliodonio phenolates resulting from the reaction of 1,3-dihydroxy benzene derivatives and (diacetoxyiodo)benzene were isolated and characterized. The new phenolates afforded cyclization products from their photochemical reaction with alkenes and alkynes and phenyl ethers from their thermal rearrangement. A possible reaction pathway is proposed in order to explain the regioselectivity of these reactions.

INTRODUCTION

The general term zwitterionic iodonium compounds, ZIC, is used for several types of hypervalent iodine compounds in which iodine is linked with two ligands and bears a positive charge internally compensated by a negative charge. The literature of ZIC, as well as of other classes of hypervalent iodine compounds up to 1991 has been reviewed by Varvoglis[1].

The most important types of ZIC are aryliodonium ylides and 2-aryliodoniophenolates.The term aryliodonium ylides refers to 1,2 dipoles with the formal negative charge on carbon, 1, whereas aryliodoniophenolates are 1,4 dipoles with the negative charge on the oxygen atom of a phenolic group, 2. In both cases the presence of electron withdrawing groups is necessary for the stabilization of the zwitterions.



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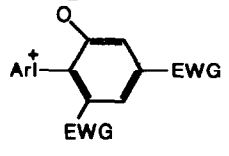
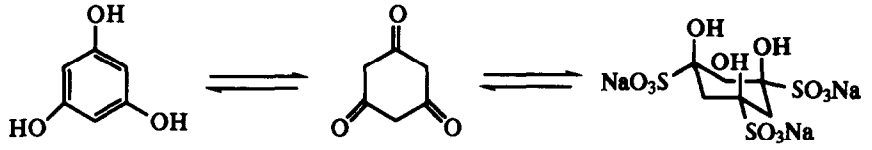


2

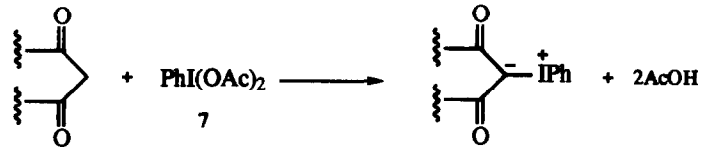
Continuing the exploration of the chemistry of aryliodonium ylides[2] and aryliodoniophenolates[3] we investigated the possibility of forming iodonium zwitterionic compounds from resorcinol or phloroglucinol derivatives. 1,3-Dihydroxy- and 1,3,5-trihydroxybenzene derivatives were selected as possible zwitterionic iodonium candidates because of their potential ability to exist in equilibrium with

their keto forms. In the case of phloroglucinol the tautomerism between the enol form **3** and the keto form **4** is supported by the formation of the tris(sodium bisulfite) adduct, **5** [4].



3 **4** **5**

The keto form **4** has three active methylene groups, which are in proper positions for the insertion of the phenyliodonio moiety, as it is well known from the formation of phenyliodonium ylides **8** from β-dicarbonyl compounds **6** and (diacetoxyiodo)benzene, DIB, **7**.

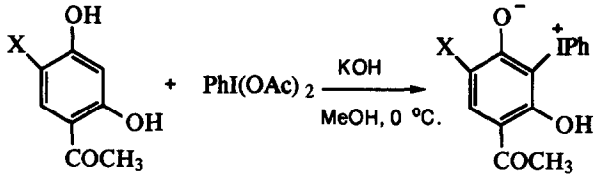


6 **8**

Moreover, there are no references in the literature about the reaction of resorcinol or phloroglucinol derivatives with hypervalent iodonium reagents. In contrast, the reaction of monohydric phenols and benzene 1,2 and 1,4 diols with a variety of hypervalent iodonium compounds, leading mostly to oxidation products, has been extensively studied[5].

RESULTS AND DISCUSSION

Resorcinol and its simple 4-substituted derivatives gave complicated mixtures of products, upon the reaction with DIB and under a variety of conditions. In the case of 2,4-dihydroxyacetophenone and derivatives **9** we were able to isolate the corresponding phenyliodoniophenolates **10**.



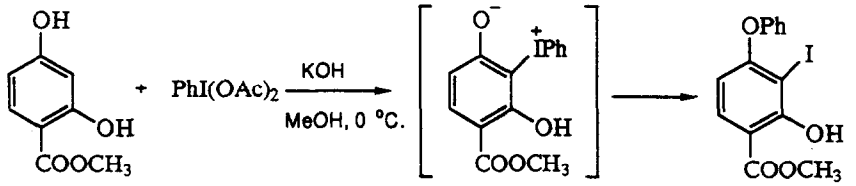
9 a, X = H
b, X = $COCH_3$
c, X = NO_2

10 a, 40%
b, 40%
c, 45%

Optimum yields of **10** were obtained when the reaction was carried out with equimolecular quantities of 2,4 -dihydroxyacetophenone and DIB , in a basic methanolic solution at 0 °C. Phenolates **10** were isolated by adjusting the pH of the resulting solution to 6-7. The same phenolates **10** were isolated

from a transylidation reaction of dihydroxyacetophenones **9** with tosyliminoiodobenzene **11** , but the yields were generally lower.

When the acetyl group in **9a** was replaced by a methoxycarbonyl group the only isolable product from the reaction of ester **12** with DIB was the iodoether **14**. The latter undoubtedly results from the thermal rearrangement of the intermediary unstable phenolate **13**. This is an indication that the acetyl group in **9** plays important role for the stabilization of phenolates **10**.

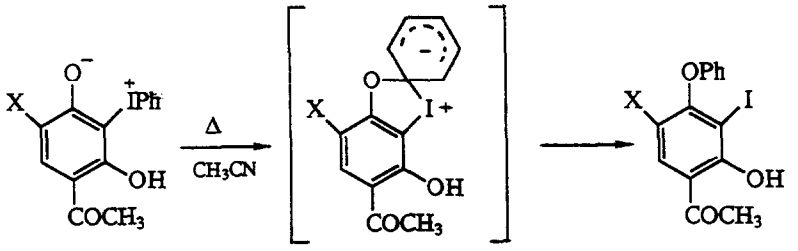


12 **13** **14**

It must be noted that the intermediacy of phenyliodoniophenolates was proposed in the reaction of substituted dihydroxyacetophenones with DIB[6], from which the only isolable products were iodoethers analogous to **14**.

Phenolates **10** are yellow non-crystalline solids which can be stored for periods up to four weeks at 5 °C without apparent decomposition. They exhibit spectroscopic data consistent with their structure. In their mass spectra the molecular ion is of high intensity, which is rather unusual for such compounds.

Upon heating, phenolates **10** are completely converted to the corresponding iodoethers **16**, probably through an intermediary spiro-Meisenheimer complex **15**, in a migration observed also in other arylioiodoniophenolates[7].

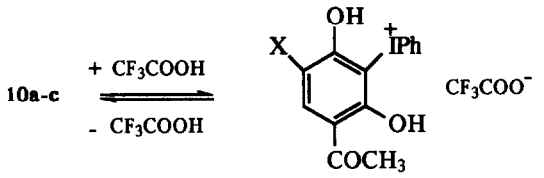


10a-c **15a-c** **16a-c**

The migration of the phenyl group takes place to the oxygen *para* to the acetyl group, as only one of the two possible isomers, in the case of **10a** and **10c** is formed. This is an indication that the structure with the formal negative charge on that specific oxygen, in phenolates **10a** and **10c**, represents the real situation of the molecule.

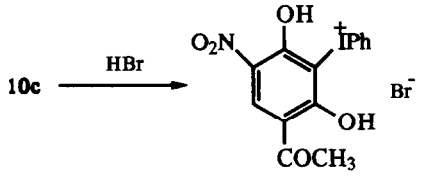
The migration of the phenyl group in phenolates **10a** and **10b** takes place even at room temperature, when they are in solution. Phenolate **10c** is relatively stable and was used for the study of reactivity.

Phenyliodoniophenolates **10** easily gave the corresponding iodonium salts upon treatment with trifluoroacetic acid in a reversible reaction.



17a-c

Phenolate **10c** reacted in the same manner with other electrophiles.



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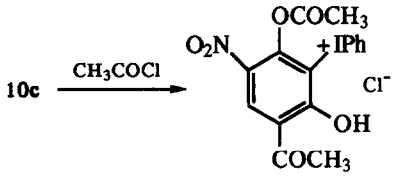
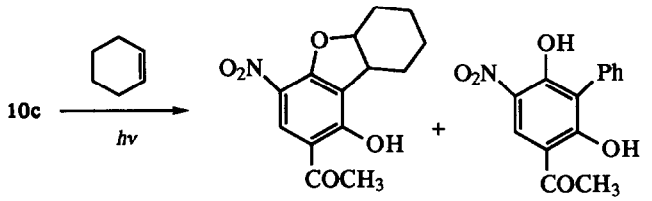


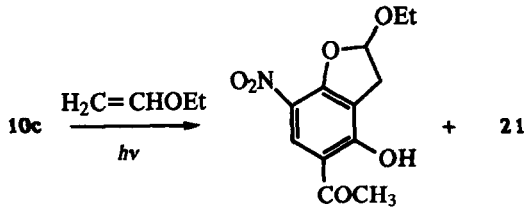
19

The thermal reaction of **10c** with alkenes and alkynes led to iodophenyl ether **16c**, but cyclization products were obtained under photolytic conditions.

Irradiation of **10c** in the presence of alkenes and enol ethers afforded the corresponding dihydrofurans **20**, **22** and **23** in low yields.



20 **21**



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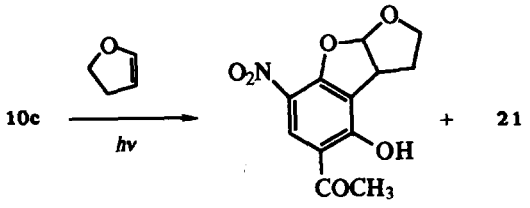
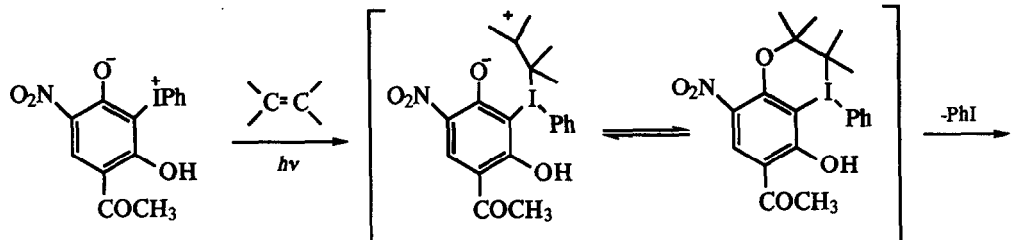
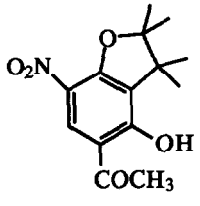


23

Again the cyclization took place exclusively on the oxygen *ortho* to nitro group. It is possible that the reaction proceeds through the intermediacy of iodanes **24**, as it is usually the case in analogous reactions of iodonium ylides with dipolophiles. This reaction pathway explains the regioselectivity in the formation of dihydrofurans.



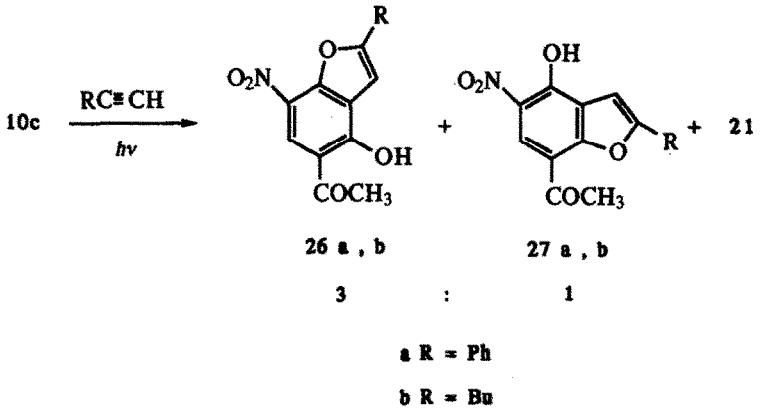


25

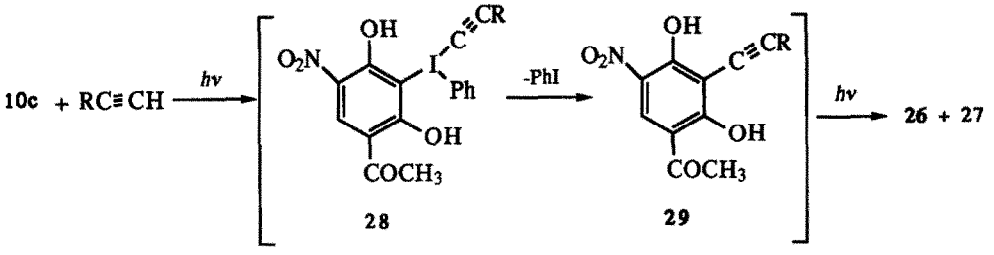
3-Phenyl-5-nitro-2,4-dihydroxyacetophenone **21** is always a by-product of the reaction. Its formation can be explained from the reaction of **10c** with phenyl radicals, resulting from the dissociation

of iodobenzene, another by-product of the reaction. When **10c** was irradiated in a benzene suspension **21** was obtained in 65% yield.

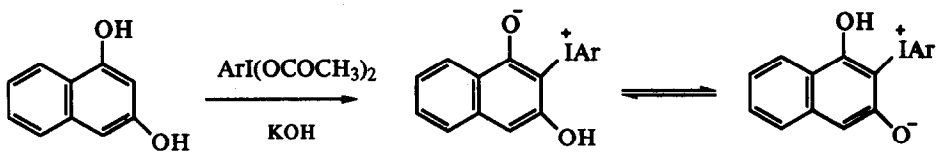
Irradiation of **10c** in the presence of terminal alkenes gave inseparable mixtures of the corresponding furans **26a**, **27a** and **26b**, **27b** (only **26a** was isolated and characterized). The ratio of the regio isomers was 3 : 1 in both cases.



A possible explanation for the formation of both regioisomers involves the intermediacy of an iodane of type **28**, which occurs with the simultaneous protonation of anionic oxygen. Iodane **28** with expulsion of iodobenzene can be converted to **29**, which can be cyclized to both isomers **26** and **27**, in a different ratio.



Another 1,3-dihydroxy compound, without a stabilizing acetyl group, 1,3-dihydroxynaphthalene **30** gave also the phenolates **31a** and **31b**.



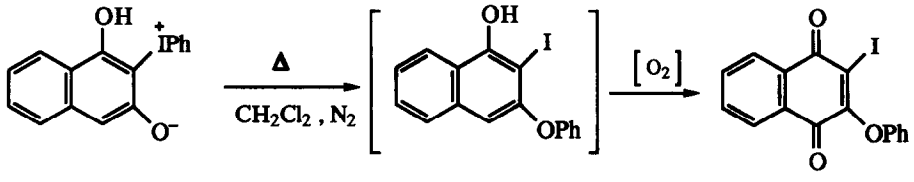
30

31 a , b

a Ar = Ph

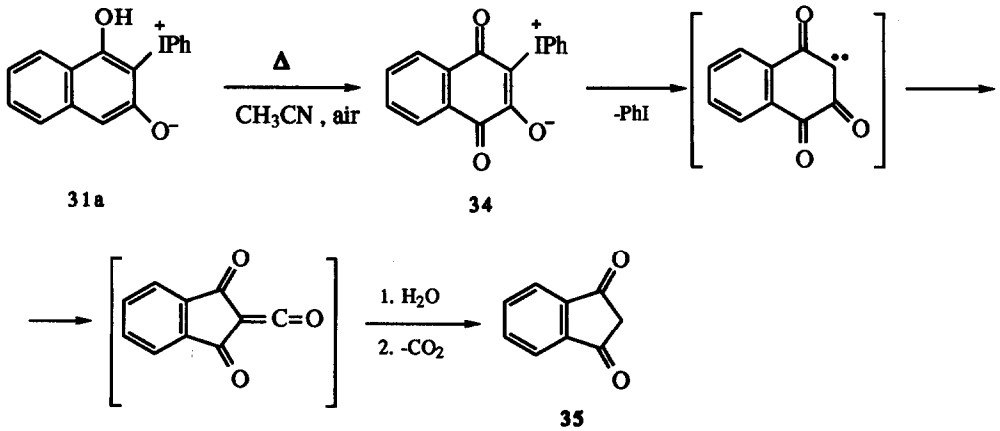
b Ar = p-tolyl

Phenolates **31** under photochemical conditions gave complicated mixtures of products along with unreacted starting material, but when a solution of **31a** in CH_2Cl_2 was refluxed under N_2, the main product was the quinone iodoether **33**, probably resulting from the oxidation of unstable iodoether **32** during work-up.



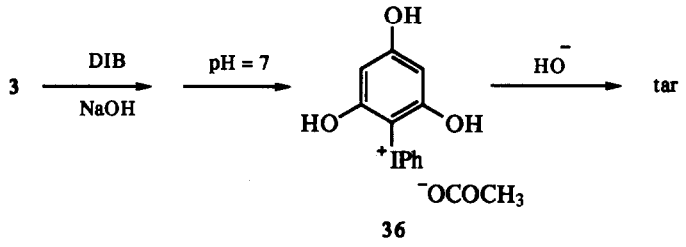
31a 32 33

This assumption is strengthened by the fact that if the same reaction is carried out in refluxing acetonitrile in atmospheric air, the main product is indanedione **35**. It is probable that phenolate **31a** is oxidised to 3-(phenyliodonio)-1,2.4-trioxo-1,2,3,4-tetrahydronaphthalenide **34**, which is converted to 1,3-indanedione **35** through the intermediacy of carbenes in a Wolff-rearrangement type pathway. The conversion of **34** to 1,3-indanedione in 91% yield has already been observed in an intependent reaction under the same conditions[8].



31a 34 35

Finally, phenyliodoniophenolates could not be isolated from the reaction of phloroglucinol **3** and nitro-phloroglucinol with DIB under a variety of conditions (solvent, temperature, rate of DIB addition etc.). The only isolable product in the case of phloroglucinol was the rather unstable phenyl iodonium salt **36**. All attempts to eliminate acetic acid from **36** under strong alkaline conditions led to tar.



36

EXPERIMENTAL

Melting points are uncorrected. IR spectra were obtained in Nujol. ^{1}H- NMR , were recorded with 80 and 300-MHz instruments with $CDCl_3$ as solvent and $SiMe_4$ as an internal standard. MS spectra were obtained with an electron beam operating at 70 eV. Irradiations were performed with a 250-Watt low-pressure Hg lamp.

Preparation of phenolates 10. A solution of (diacetoxyiodo)benzene **7** (1 mmol) in methanol (5 ml) was added to to a solution of the corresponding dihydroxyacetophenone **9a-c** (1 mmol) and KOH (3mmol) in methanol (10 ml) at 0 °C. After 30 min at 0 °C, cold water (30 ml) was added and the resulting solution was cautiously acicified to pH 6-7 with ice-cold dilute hydrochloric acid. The solution was thrice extracted with cold CH_2Cl_2 and the combined organic solvent, after drying (MgSO4, 30 min, 0 °C), was removed in vacuo. The resulting slurry was digested with 10 ml of absolute ether and phenolates **10** were precipitated. In the case of **10c** the phenolate can be isolated by filtration after the acidification of the methanolic solution.

4-Acetyl-3-hydroxy-2-phenyliodonio-phenolate, 10a; yield 40%, mp 81-85° C; IR 3400, 1595 cm^{-1}; ^{1}H-NMR δ 2.32 (s, 3H), 6.15 (d, 1H , J=9Hz), 7.03 (m, 6H), 13.60 (s, 1H, OH); MS m/z (rel. intensity) 354 (M^+ 96), 337 (16), 204 (20), 43 (100). Anal. Calcd for $C_{14}H_{11}IO_3$: C, 47.46; H, 3.1%. Found: C, 46.92; H, 2.85%.

4,6-Diacetyl-3-hydroxy-2-phenyliodonio-phenolate, 10b; yield 40%, mp 120-130° C; IR 3400, 1640, 1605 cm^{-1}; ^{1}H-NMR δ 2.40 (s, 6H), 6.95 (m, 3H), 7.30 (m , 2H), 8.25 (s, 1H); MS m/z (rel. intensity) 396 (M^+, 82) , 380 (11), 302 (100), 204 (28). Anal. Calcd for $C_{16}H_{13}IO_4$: C, 48.48; H, 3.28%.. Found: C, 48.37; H, 3.31%.

4-Acetyl-3-hydroxy-6-nitro-2-phenyliodonio-phenolate, 10c; yield 45%, mp 145-147° C; IR 3400, 1610, 1540, 1530, 1370 cm^{-1}; ^{1}H-NMR δ 2.45 (s, 3H), 7.40 (m, 3H), 8.00 (m, 2H), 8.60 (s, 1H); MS m/z (rel. intensity) 399 (M^+, 6) , 306 (16), 272 (15), 204 (33), 179 (15), 77 (100), 43 (88). Anal. Calcd for $C_{14}H_{10}INO_5$: C, 42.10; H, 2.50; N, 3.51 %. Found: C, 42.37; H, 2.45; N, 3.68%.

Alternative preparation of phenolates 10. A solution of the corresponding acetyl resorcinol **10a-c** (2 mmol) in CH_2Cl_2 (3 ml) was added to a solution of tosyliminoiodobenzene **11**[9] (2 mmol) in CH_2Cl_2 (3 ml) at -5 °C. The precipitated tosylamide was removed by filtration, absolute ether (30 ml) was added and the phenolate **10** was precipitated and isolated. **10a** yield 30%, **10b** yield 28%, **10c** yield 30% .

Methyl-(2-hydroxy-3-iodo-4-phenoxy)benzoate, 14. On attempted preparation of the corresponding phenolate from methyl-(2,4-dihydroxy)benzoate **12** and **7** (under the previously described conditions) the only isolable product was the ester **14**. Yield 56%, mp 65° C (hexane); IR 3400, 1720, 1670, 1585, 1260 cm^{-1}; ^{1}H-NMR δ 3.92 (s, 3H), 6.27, (d, 1H, J=10Hz), 6.96-7.51 (m, 5H), 7.73 (d, 1H, J=10Hz), 11.88 (s, 1H, OH); MS m/z (rel. intensity) 370 (M^+, 100), 338 (55), 242 (35), 211 (65), 183(30), 149 (37), 137 (63). Anal. Calcd for $C_{14}H_{11}IO_4$: C, 45.43; H, 2.99%. Found: C, 45.31; H, 3.08%.

Thermal rearrangement of phenolates 10. A suspension of the appropriate phenolate **10a-c** (1 mmol) in CH_3CN was refluxed for 30 min. The resulting clear solution was concentrated and chromatographed on column (silica gel, hexane-CH_2Cl_2 2:1 as eluant) to afford the corresponding iodoether**16a-c.** Recrystalization from hexane. Similar results were obtained by refluxing solutions of phenolates in CH_2Cl_2.

2-Hydroxy-3-iodo-4-phenoxy-acetophenone, 16a; yield 70%, mp 72° C; IR 3400, 1625, 1580 cm^{-1}; ^{1}H-NMR δ 2.60 (s, 3H) , 6.25 (d, 1H , J=9Hz), 7.30 (m, 5H), 7.60 (d, 1H, J=9Hz), 13.60 (s, 1H, OH); MS m/z (rel. intensity) 354 (M^+, 100), 339 (67), 227 (53), 43 (16). Anal. Calcd for $C_{14}H_{11}IO_3$: C, 47.46; H, 3.11% . Found: C, 47.70; H, 3.33%.

2-Hydroxy-3-iodo-4-phenoxy-5-acetyl-acetophenone, 16b; yield 50%, mp 132-136° C ; IR 3400, 1675, 1635, 1580 cm^{-1}; ^{1}H-NMR δ 2.45 (s, 3H), 2.65 (s, 3H), 6.70 - 7.05 (m, 5H), 8.45 (s, 1H) , 13.80 (s, 1H , OH); MS m/z (rel. intensity) 396 (M^+, 100), 380 (17), 305 (28), 77 (55). Anal. Calcd for $C_{16}H_{13}IO_4$: C, 48.48 ; H, 3.28%. Found: C, 48.47; H, 3.12%.

2-Hydroxy-3-iodo-4-phenoxy-5-nitro-acetophenone, 16c; yield 47%, mp 180-185° C ; IR 3400, 1635, 1580, 1525, 1370 cm^{-1}; ^{1}H-NMR δ 2.70 (s, 3H), 6.70 (m, 2H), 7.30 (m, 3H), 8.00 (s, 1H) , 13.60 (s, 1H, OH); MS m/z (rel. intensity) 399 (M^+, 6), 306 (16), 272 (18), 176 (46), 77 (31). Anal. Calcd for $C_{14}H_{10}INO_5$: C, 42.10; H, 2.50; N, 3.51%. Found: C, 41.90; H, 2.60; N, 3.29%.

Preparation of trifluoroacetates of phenolates 10. The phenolate (0.25 mmol) was dissolved in CH_2Cl_2 (10 ml) and CF_3COOH (1 ml) was added. After 15 min at room temperature the solution was washed with H_2O, dried, concetrated till a small volume and the corresponding trifluoroacetate was crystallized upon the addition of a mixture of ether-hexane 1:1 (20 ml).

2,6-Dihydroxy-3-acetyl-phenyliodonium trifluoroacetate, 17a; yield 30%, mp 120-125° C; IR 1600, 1570 cm^{-1}; ^{1}H-NMR δ 2.50 (s, 3H), 6.90 (d, 1H, J=9Hz), 7.2-8.2 (m, 6H); MS m/z (rel. intensity) 354 (6), 337 (25), 204 (32). Anal. Calcd for $C_{16}H_{12}F_3IO_5$: C, 41.04; H, 2.59%. Found: C, 40.93; H, 2.51%.

2,6-Dihydroxy-3,5-diacetyl-phenyliodonium trifluoroacetate, 17b; yield 32% , mp 110-115° C; IR 1650, 1570 cm^{-1}; ^{1}H-NMR δ 2.63 (s, 6H), 7.50 (m, 3H), 8.00 (m , 2H), 8.39 (s, 1H) ; MS m/z (rel. intensity) 396 (15), 381 (25), 303 (100), 204 (35). Anal. Calcd for $C_{18}H_{14}F_3IO_6$: C, 42.37; H, 2.76% . Found: C, 42.48; H, 2.68%.

2,6-Dihydroxy-3-acetyl-5-nitro-phenyliodonium trifluoroacetate, 17c; yield 52%, mp 120° C; IR 3200, 1640, 1560, 1530, 1370 cm^{-1}; ^{1}H-NMR δ 2.70 (s, 3H), 7.80 (m, 3H), 8.20 (m , 2H), 8.90 (s, 1H); MS m/z (rel. intensity) 399 (13), 306 (15), 272 (29), 204 (38), 179 (62), 77 (100). Anal. Calcd for $C_{16}H_{11}F_3INO_7$: C, 37.45; H, 2.16; N, 2.73%. Found: C, 37.78; H, 2.00; N, 2.60%.

Reaction of phenolate 10c with HBr. Hydrobromic acid (d=1.42, 1 ml) was added to a solution of **10c** (1 mmol) in CH_3CN (10 ml) and the solution was stirred at room temperature for 24 h. After removal of the solvent and addition of ether, **2,6-dihydroxy-3-acetyl-5-nitro-phenyliodonium-bromide 18** crystallized; yield 87%, mp 180° C; IR 3160, 1610, 1550, 1370 cm^{-1}; ^{1}H-NMR δ 2.80 (s, 3H), 7.40 (m, 3H), 8.10 (m , 2H), 8.80 (s, 1H); MS m/z (rel. intensity) 399 (52), 306 (23), 204 (5), 77 (100). Anal. Calcd for $C_{14}H_{11}BrINO_5$: C, 35.00; H, 2.29 N, 2.92%. Found: C, 34.88; H, 2.18; N, 3.08%.

Reaction of phenolate 10c with acetyl chloride. Acetyl chloride (1 mmol) was added to a solution of **10c** (0.75 mmol) in CH_2Cl_2 (10 ml) and the solution was stirred at room temperature for three hours. Removal of the solvent and addition of hexane gave **2-acetoxy-3-nitro-5-acetyl-6-hydroxy-phenyliodonium chloride 19**; yield 35%, mp 170° C; IR 3180, 1635, 1550 cm^{-1}; ^{1}H-NMR ($CDCl_3$ + CF_3COOH) δ 1.95 (s, 3H), 2.70 (s, 3H), 7.20 (m, 3H), 7.70 (m, 2H), 8.64 (s, 1H); MS m/z (rel. intensity) 442 (M^+-Cl, 18), 399 (12), 306 (45), 272 (29), 179 (100), 94 (4). Anal. Calcd for $C_{16}H_{13}ClINO_6$: C, 40.17; H, 2.72 ; N, 2.93%. Found: C, 39.88; H, 2.75; N, 3.13%.

Photoreactions of 10c with alkenes and alkynes. A solution of phenolate **10c** (1 mmol) and the appropriate alkene or alkyne (3-5 mmol) in CH_2Cl_2 (5 ml) and CH_3CN (5 ml) was irradiated for 4 hours. The solution was concentrated and chromatographed on column (silica gel, hexane-CH_2Cl_2 1:1 as eluant). The first fractions were chromatographed again (silica gel, hexane-acetone 1:1). Iodobenzene, ether **16c** and **3-phenyl-5-nitro-2,4-dihydroxy-acetophenone 21** were always products of the reaction. The latter was isolated in yields of 20-30%. When a suspension of **10c** in benzene was irradiated, **21** was the only isolable product in 65% yield; mp 160-161° C; IR 1630, 1600, 1520, 1370 cm^{-1}; ^{1}H-NMR δ 2.70 (s, 3H), 7.40 (s br , 5H), 8.70 (s, 1H), 12.40 (s,1H, OH), 13.30 (s, 1H, OH); MS m/z (rel. intensity) 273 (M^+, 100), 258 (62), 256 (74), 212 (31), 226 (42). Anal. Calcd for $C_{14}H_{11}NO_5$: C, 61.54; H, 4.03; N, 5.13%. Found: C, 61.33; H, 3.87; N, 5.29%.

Reaction with cyclohexene, to give **2-acetyl-4-nitro-7,12-dihydro-cyclohexano[d]-benzo[b]-furan-1-ol, 20;** yield 12%, oil; IR 3080, 1630, 1610 cm^{-1}; ^{1}H-NMR δ 1.2-2.4 (m, 6H), 2.70 (m,3H) , 3.70 (m,1H), 8.60 (s, 1H), 13.17 (s, 1H, OH); MS m/z (rel. intensity) 277 (M^+,12), 260 (100), 242 (8, 230 (25), 43 (35). Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.65 ; H, 5.41; N, 5.05%. Found: C, 61.03 ; H, 5.67; N, 4.82%.

Reaction with ethyl-vinyl-ether, to give **2-acetyl-4-nitro-7-ethoxy-7,8-dihydro--benzo[b]-furan-1-ol 22;** yield 19%, mp 67-70° C; IR 3100, 1625, 1580, 1525, 1370 cm^{-1}; ^{1}H-NMR δ 1.2 (t, 3H, J=7 Hz), 2.55 (s, 3H), 3.20 (m, 2H), 3.90 (m , 2H), 6.01 (dd, 1H), 8.55 (s, 1H), 12.09 (s, 1H, OH) ; MS m/z (rel. intensity) 267 (M^+, 100), 222 (33), 193 (97), 175 (13). Anal. Calcd for $C_{12}H_{13}NO_6$: C, 53.93; H, 4.90; N, 5.24%. Found: C, 54.17 ; H, 4.78; N, 4.94%.

Reaction with 2,3-dihydrofuran, to give **2-acetyl-4-nitro-7,9,10,11-tetrahydro-furano[3,4-d]-benzo[b]-furan-1-ol, 23;** yield 15%, oil; IR 3080, 1630, 1610, 1580, 1370 cm^{-1}; ^{1}H-NMR δ 2.28 (m, 2H), 2.61 (s, 3H), 3.69 (m,1H), 4.12 (m, 2H), 6.62 (1H, d, J=6Hz), 8.53 (s, 1H), 13.03 (s,

1H, OH) ; MS m/z (rel. intensity) 265 (M^+, 100), 247 (23), 218 (40), 131 (25), 69 (90) 43 (100). Anal. Calcd for $C_{12}H_{11}NO_6$: C, 54.34; H, 4.18; N, 5.28%. Found: C, 54.11; H, 4.28; N, 5.49%.

Reaction with phenyl acetylene. From the reaction a 3:1 mixture of the two isomers **26a** and **27a** in 13% yield was isolated. Chromatography was repeated and pure **2-acetyl-4-nitro-7-phenyl-benzo[b]-furan-1-ol, 26a** was isolated; mp 167° C; IR 3080, 1630, 1605, 1520, 1370, 1290 cm^{-1} ; ^{1}H-NMR δ 2.70 (s, 3H), 7.30 (m, 6H), 8.70 (s, 1H), 14.10 (s, 1H, OH); MS m/z (rel. intensity) 297 (M^+, 20) , 183 (30), 149 (35), 105 (100), 77 (78), 43 (55). Anal. Calcd for $C_{16}H_{11}NO_5$: C, 64.65; H, 3.70; N, 4.71% . Found: C, 64.88 ; H, 4.00; N, 4.51%.

The other isomer **4-acetyl-2-nitro-7-phenyl-benzo[b]-furan-1-ol, 27a** has ^{1}H-NMR δ 2.89 (s, 3H), 7.30-7.80 (m , 6H), 8.62 (s, 1H), 13.00 (s, 1H, OH), as it is deduced from the spectrum of the mixture **26a** and **27a**.

Reaction with 1-hexyne. From the reaction an inseparable 3:1 mixture of **2-acetyl-4-nitro-7-butyl-benzo[b]-furan-1-ol, 26b** and **4-acetyl-2-nitro-7-butyl-benzo[b]-furan-1-ol , 27b** was isolated. ^{1}H-NMR δ 14.08 (s, 1H, OH) for **26b** and 13.00 (s, 1H, OH) for **27b**. MS m/z (rel. intensity) 277 (M^+, 100), 262 (51), 234 (60).

Preparation of naphtholates 31a and 31b. Potassium hydroxide (2 mmol), dissolved in 5 ml of methanol, was added to a solution of 1,3-dihydroxynaphthalene **30** (1 mmol) in methanol (5 ml) at 0 °C. A solution of (diacetoxyiodo)arene (1 mmol) in methanol (5 ml) was added and the solution kept at 0 °C for 30 min. Icy water was added - the pH of the solution must be 6.5-7 - and the resulting suspension was extracted twice with cold CH_2Cl_2.The combined organic layers were dried and concentrated till a small volume. Naphtholates **31a** and **31b** were precipitated upon the addition of a mixture of ether-hexane.

2-Phenyliodonio-3-hydroxy-1-naphtholate (or 2-phenyliodonio-1-hydroxy-3-naphtholate), 31a; yield 30%, mp 85-90° C; IR 3300(br), 1680,1580,1530 cm^{-1}; ^{1}H-NMR δ 7.25 (m, 4H), 7.72 (m, 4H), 8.19 (m, 2H); MS m/z (rel. intensity) 204 (55), 174 (87), 163 (58), 146 (45), 105 (100), 77 (92). Anal. Calcd for $C_{16}H_{11}IO_2$: C, 53.03 ; H, 3.03% . Found: C, 53.11 ; H, 3.00 %.

2-(p-Tolyliodonio)-3-hydroxy-1-naphtholate (or 2-(p-tolyliodonio-1-hydroxy-3-naphtholate), 31b; yield 28%, mp 95° C; IR 3300(br), 1680,1580,1530 cm^{-1}; ^{1}H-NMR δ 2.23 (s, 3H), 6.85 (d, 2H , J=10 Hz), 7.58 (d, 2H, J=10 Hz), 7.79 (m, 3H), 8.12 (m, 2H); MS m/z (rel. intensity) 218 (78), 174 (8), 146 (12), 91 (100), 76 (15). Anal. Calcd for $C_{17}H_{13}IO_2$: C, 54.25; H, 3.45%. Found: C, 54.39; H, 3.53% .

Thermal rearrangement of 31a. A solution of naphtholate **31a** (1 mmol) in dry CH_2Cl_2 (10 ml) was refluxed under N_2 for 2 hrs. The resulting solution was concentrated and chromatographed on column (silica gel-hexane-CH_2Cl_2 as eluant) to afford **2-Iodo-3-phenoxy-1,4-naphthoquinone, 33** ; yield 10%, mp 135° C; IR 1660, 1580,1565, 1260 cm^{-1}; ^{1}H-NMR δ 6.98 (m, 2H), 7.34 (m, 3H), 8.01 (m, 2H), 8.19 (m, 2H); MS m/z (rel. intensity) 376 (M^+,100), 249 (60), 221 (28), 193 (18), 165 (30), 77 (95). Anal. Calcd for $C_{16}H_9IO_3$: C, 51.09; H, 2.41 %. Found: C, 50.74 H, 2.58%.

A solution of naphtholate **31a** (1 mmol) in CH_3CN (10 ml) was refluxed for 2 hrs. After the usual work-up the only isolable product was **1,3-indanedione 35**, mp 126-128° C, identical in all respects with an authentic sample of 1,3-indanedione.

Reaction of phloroglucinol 3 with (diacetoxyiodo)benzene. A solution of NaOH (3 mmol) in methanol (5 ml) was added to a solution of phloroglucinol (1 mmol) in methanol 5 (ml) and the solution was stirred at r.t. for 1 hr. A solution of (diacetoxyiodo)benzene, (3 mmol) in methanol (5 ml) was added to the first solution followed by the addition of 3 mmol of NaOH in 5 ml of methanol. After 30 min the final solution was diluted with water and extracted with CH_2Cl_2 to afford **(2,4,6-trihydroxy-phenyl)-phenyl-iodonium acetate, 36;** yield 21%, mp 85-90° C; IR 3350, 1615, 1580, 1525 cm^{-1}; ^1H-NMR δ 2.15 (s, 3H), 6.98 (m, 2H), 3.40-4.00 (2 br, 3H), 7.05-7.40 (m, 5H), 7.78 (m, 2H); MS m/z (rel. intensity) 329 (M^+- CH_3COO, 15), 204 (37), 142 (95), 127 (40), 94 (15), 77 (33), 44 (100). No satisfactory elemental analysis could be obtained.

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