1 H, H-9), 7.23 (ddd, J = 7.8, 7.2, 2.0 Hz, 1 H, H-11), 7.69 (d, J = 7.8 Hz, 1 H, H-12).

Methyl 2,16-Didehydrotubifolidine-1-carboxylate (45). To a solution of **44** (80 mg, 0.2 mmol) in absolute EtOH (6 mL) was added Raney Ni (W-2, 3 spatulas). After the mixture was refluxed for 1.5 h no trace of **44** was detected by TLC. The solids were removed by filtration and washed with EtOH. Removal of the solvent and purification of the residue by flash chromatography (95:5 Et_2O–DEA) gave **45** (28 mg, 45%): IR ($CHCl_3$) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (t, J = 7.2 Hz, 3 H, H-18), 1.27 (m, 2 H, H-19), 1.48 (ddd, J = 12.8, 3.8, 2.8 Hz, 1 H, H-14R), 1.63 (dd, J = 11.3, 7.0 Hz, 1 H, H-6α), 1.70 (m, 1 H, H-20α), 1.94 (dt, J = 12.8, 2.7 Hz, 1 H, H-14S), 2.11 (t, J = 11.6 Hz, 1 H, H-21β), 2.51 (m, 1 H, H-15α), 2.75 (dd, J = 14.6, 7.6 Hz, 1 H, H-5β), 2.75–3.00 (masked, 1 H, H-6β), 2.89 (dd, J = 11.6, 4.5 Hz, 1 H, H-21α), 3.00 (td, J = 14.6, 7.0 Hz, 1 H, H-5α), 3.78 (br s, 1 H, H-3α), 3.90 (s, 3 H, CH_3O), 5.98 (d, J = 8.0 Hz, 1 H, H-16), 7.04 (td, J = 7.4, 1.2 Hz, 1 H, H-10), 7.11–7.24 (m, 2 H, H-9 and H-11), 7.75 (d, J = 8.0 Hz, 1 H, H-12). Anal. Calcd for $C_{20}H_{24}N_2O_3 \cdot H_2O$: C, 70.15; H, 7.65; N, 8.18. Found: C, 70.27; H, 8.00; N, 7.90.

(±)-Tubifoline (46). A solution of **45** (32 mg, 0.1 mmol) in 1 N NaOMe in MeOH (0.4 mL) was refluxed for 1 h. The mixture was poured into ice-cold H_2O (5 mL) and extracted with CH_2Cl_2. The extracts were washed with brine, dried, and evaporated to give a solid which, after purification by flash chromatography (95:5 Et_2O–DEA), afforded (±)-tubifoline (**46**) (21 mg, 80%): ^1H NMR ($CDCl_3$) δ 0.95 (t, J = 7.2 Hz, 3 H, H-18), 1.18 (ddd, J = 13.8, 4.4, 2.4 Hz, 1 H, H-14R), 1.31 (m, 2 H, H-19), 1.63 (ddd, J = 13.8, 3.4, 2.2 Hz, 1 H, H-14S), 1.75 (m, 1 H, H-20α), 1.93 (ddd, J = 13.5, 5.5, 1.3 Hz, 1 H, H-6α), 2.36 (m, 1 H, H-15α), 2.55 (t, J = 12.5 Hz, 1 H, H-21β), 2.59 (d, J = 14.6 Hz, 1 H, H-16β), 2.78 (ddd, J = 13.5, 12.0, 7.0 Hz, 1 H, H-6β), 2.84 (dd, J = 14.6, 10.5 Hz, 1 H, H-16α), 3.10–3.20 (masked, 1 H, H-5β), 3.14 (dd, J = 12.5, 4.6 Hz, 1 H, H-21α), 3.25 (td, J = 12.0, 5.5 Hz, 1 H, H-5α), 3.75 (m, 1 H, H-3α), 7.18 (t, J = 8.0 Hz, 1 H, H-10), 7.30 (m, 2 H, H-9 and H-11), 7.53 (d, J = 8.0 Hz, 1 H, H-12); ^{13}C NMR ($CDCl_3$) Table II. TLC, IR, UV, and MS were identical with those reported for the natural product.[7,41,43d]

(±)-19,20-Dihydroakuammicine (47). A solution of **45** (91 mg, 0.3 mmol) in MeOH (40 mL) was photolyzed under argon with a 125-W high-pressure mercury lamp in a quartz immersion well reactor for 1 h. Evaporation of the solvent gave a residue which was chromatographed. On elution with 97:3 $CHCl_3$–MeOH, (±)-tubifoline (**46**, 12 mg, 13%), (±)-19,20-dihydroakuammicine (**47**, 19 mg, 20%), and starting material (**45**, 20 mg) were isolated successively. The R_f of **47** with several solvent mixtures were coincident with those reported[41,43d] for the natural product, and a deep blue color appeared with cerium(IV) sulfate. **47**: ^1H NMR ($CDCl_3$) δ 0.90 (m, 3 H, H-18), 0.95 and 1.25 (2 m, 2 H, H-19), 1.40 (dt, J = 12.5, 3.0 Hz, 1 Hz, H-14R), 1.85 (m, 1 H, H-20α), 1.95 (dd, J = 12.5, 6.8 Hz, H-6α), 2.05 (t, J = 12.5 Hz, 1 H, H-21β), 2.06 (dt, J = 12.5, 3.0 Hz, 1 H, H-14S), 2.80–3.00 (m, 2 H, H-5β and H-6β), 3.00 (dd, J = 12.5, 6.5 Hz, 1 H, H-21α), 3.10 (td, J = 12.0, 6.8 Hz, 1 H, H-5α), 3.15 (m, 1 H, H-15α), 3.75 (s, 3 H, CH_3O), 3.95 (br s, 1 H, H-3α), 6.80 (d, J = 7.5 Hz, 1 H, H-12), 6.89 (t, J = 7.5 Hz, 1 H, H-10), 7.12 (t, J = 7.5 Hz, 1 H, H-11), 7.15 (d, J = 7.5 Hz, 1 H, H-9), 9.03 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) Table II.

Acknowledgment. This work was supported by the DGICYT (projects PB87-0062 and PB88-0316), Spain.

Registry No. (±)-**1**, 99552-97-3; (±)-**2a**, 101481-26-9; (±)-**2b**, 128902-24-9; (±)-**3a**, 101491-90-1; (±)-**3b**, 128902-25-0; (±)-**4a** (isomer 1), 101481-17-8; (±)-**4a** (isomer 2), 101491-91-2; (±)-**4b** (isomer 1), 101481-29-2; (±)-**4b** (isomer 2), 101481-20-3; (±)-**5a**, 128902-16-9; (±)-**5b**, 128902-26-1; (±)-**6a** (isomer 1), 101481-19-0; (±)-**6a** (isomer 2), 101481-28-1; (±)-**8a** (isomer 1), 128902-17-0; (±)-**8a** (isomer 2), 129029-34-1; (±)-**8b** (isomer 1), 128902-27-2; (±)-**8b** (isomer 2), 128948-97-0; (±)-**9a**, 101481-18-9; (±)-**9b**, 101678-89-1; (±)-**10a**, 101481-21-4; (±)-**10b**, 128902-28-3; (±)-**13**, 128902-18-1; (±)-**14**, 101481-22-5; (±)-**15**, 101481-27-0; (±)-**18**, 101481-24-7; (±)-**21**, 128902-19-2; **22**, 128902-20-5; (±)-**23**, 101481-23-6; (±)-**25**, 101481-16-7; (±)-**26**, 128902-21-6; (±)-**27**, 116787-64-5; **28**, 95533-03-2; (±)-**29a**, 128902-22-7; (±)-**29b**, 128948-94-7; (±)-**30a**, 123718-72-9; (±)-**30b**, 128948-95-8; (±)-**32a**, 116965-66-3; (±)-**32b**, 116965-63-0; **33**, 7023-83-8; **34**, 58925-98-7; **35**, 75272-23-0; **36**, 51534-60-2; **37**, 79414-76-9; (±)-**40**, 128902-23-8; (±)-**41a**, 128948-93-6; (±)-**41b**, 116965-65-2; (±)-**42a**, 122437-63-2; (±)-**42b**, 128948-96-9; (±)-**43a**, 20823-98-7; (±)-**43b**, 117020-72-1; (±)-**44**, 122419-45-8; (±)-**45**, 122419-46-9; (±)-**46**, 20823-97-6; (±)-**47**, 121916-34-5; $PhSCH_2COCl$, 7031-27-8; $BrCH_2CH(OEt)_2$, 2032-35-1; CH_3SCH_2COCl, 35928-65-5; $(EtO)_2CHCO_2Et$, 6065-82-3.

Polar Effects in the Decomposition of Bis(3-alkoxyaroyl) Peroxides. Synthesis of 8-Alkoxy-6*H*-dibenzo[*b*,*d*]pyran-6-ones

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The reaction of four substituted bis(3-alkoxybenzoyl) peroxides (**1b–e**) in neat phenols (**2a–e**) affords mainly 8-alkoxy-6*H*-dibenzo[*b*,*d*]pyran-6-ones (**7**) and ortho-benzoyloxylation products (**4**) of the phenol. Diaroyl peroxides without electron-releasing meta substituents afford essentially products **4**. A mechanism involving monoelectronic oxidation of the phenol by the peroxide and biaryl coupling by preferential addition of the phenol radical cation to the ortho positions to the alkoxy group of the diaroyl peroxide is suggested.

Although the oxidation of various phenols with dibenzoyl peroxide has been considerably investigated,[1,2] comparatively little work has been performed on the oxidation of phenols by bis(substituted aroyl) peroxides. The more frequently reported bis(substituted aroyl) peroxide was the strongly electrophilic 4-nitro derivative.[1] This appears surprising in view of the controversy about the mechanism of these reactions.[3]

Until now, the products of the interaction of diaroyl peroxides and phenols have been reported to be the ortho-benzoyloxylated phenols **4** (normally as an equilibrium mixture resulting from trans aroyloxylation) with ortho unsubstituted phenols, and the relatively unstable *o*-

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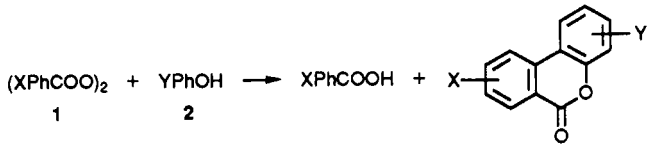
(aroyloxy) dienone (**5**) with *o*-alkyl-substituted phenols. Compounds **5** easily rearrange to the *p*-(aroyloxy) derivative[4] or to dimeric or side-chain oxidation products.[1]

Recently,[5] in a detailed study of the thermal and photochemical decomposition of dibenzoyl peroxide (**1a**) over silica gel in cyclohexane, Leffler observed an increase of the importance of the ionic over the radical mode of decomposition of the peroxide and identified a low amount (0.12–1.2%) of the previously undetected dibenzo-α-pyrone **7aa**.

We also observed low amounts of compound **7aa** (0.1%) when dibenzoyl peroxide was decomposed in neat phenol.[6] This observation prompted us to investigate the possible pathways responsible for the formation of this compound by analyzing the effect of the phenol as solvent for the decomposition of **1** and the effect of substituents of the peroxide on the yield of **7**. The unimolecular thermolysis of diaroyl peroxides shows in fact some polar character in the transition state (represented as an hybrid of singlet radical pair and ion-pair structures as suggested by Walling),[7] and the ionic contribution can become increasingly dominant with an appropriate choice of substituents.[8] The possibility to modify the polar contribution by using polar solvent, medium, or substituents suggests an important role in the solvent cage and a highly organized transition state. These conditions are frequently fulfilled also in electron-transfer reactions, and it is well documented that the oxidant diaroyl peroxides are easily involved in reduction processes by a variety of reducing agents, mainly metal salts[9] and reducing radicals.[10] Compounds **7** are interesting in this respect because they can be considered as products of selective aromatic C–C heterocoupling, a process intrinsically similar to the more common C–C homocoupling of phenols.

We soon recognized that dibenzo-α-pyrones are not always formed in trace amounts in the decomposition of diaroyl peroxides in the presence of phenols, but that these compounds account for a significant part of the reaction when bis(3-alkoxybenzoyl) peroxides (**1b–e**) are decomposed in neat phenols (**2a–e**). However, compounds **7** were always detected in combination with products **4** and low amounts of diphenol **3**.



1 2 7

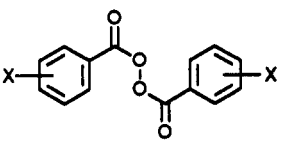
Results and Discussion

Bis(3-methoxybenzoyl) peroxide (**1b**) in neat 4-methylphenol (**2b**) is completely decomposed in 1 h at 60 °C with formation of the catechol derivative **4bb** (53%), 2,2′-dihydroxy-5,5′-dimethylbiphenyl (**3**) (16%) and pyrones **7bb** and **7′bb** in 9 and 2% yield, respectively. Under these conditions, similar product distributions were observed with other bis(3-methoxysubstituted benzoyl) peroxides and other phenols (Table I).

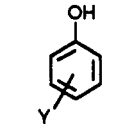
Table I. Products Distribution in the Decomposition of Diaroyl Peroxides (1a–g) in Neat Phenols (2a–g) at 60 °C

			products (yield, %)			
entry	1	2	3	4	7	8
1	**1a**	**2a**	6	82	0.1	8
2	**1a**	**2b**	13	80[a]	–	2
3	**1b**	**2b**	16	53	11[b]	2
4	**1c**	**2b**	24	28	41	tr
5	**1d**	**2b**	21	–	60	5
6	**1e**	**2b**	15	–	51	17
7	**1d**	**2c**	tr	–	64	tr
8	**1c**	**2d**	6[c]	tr	40	tr
9	**1f**	**2b**	5	71	–	20
10	**1g**	**2b**	5	70[c,d]	–	–
11	**1c**	**2g**[d,e]	–	–	–	–

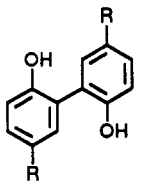
[a] Also isolated **6ab** (5%). [b] Mixture of **7bb** (9%) and **7′bb** (2%). [c] Mixture of orcine dimers. [d] An unstable yet unidentified compound was also observed. [e] A white polymer was obtained.



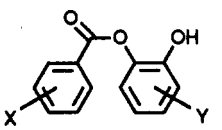
1a: X = H
b: X = 3-OMe
c: X = 3,5-(OMe)$_2$
d: X = 3,4-(OMe)$_2$
e: X = 3,4,5-(OMe)$_3$
f: X = 4-OMe
g: X = 4-NO$_2$



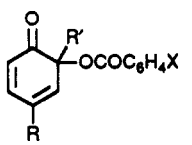
2a: Y = H
b: Y = 4-Me
c: Y = 3-Me
d: Y = 3-OH, 5-Me
e: Y = 4-OMe
f: Y = 4-OH
g: Y = 3-CH$_2$CH$_2$(3-OHPh)



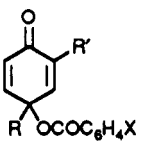
3a: R = H
b: R = Me



4aa: X = H; Y = H
ab: X = H; Y = 4-Me
bb: X = 3-OMe; Y = 4-Me
cb: X = 3,5-(OMe)$_2$; Y = 4-Me
db: X = 3,4-(OMe)$_2$; Y = 4-Me
eb: X = 3,4,5-(OMe)$_3$; Y = 4-Me
dc: X = 3,4-(OMe)$_2$; Y = 3-Me
cd: X = 3,5-(OMe)$_2$; Y = 3-OH, 5-Me



5ab: R′ = Me; X = R = H



6ab: R = Me; X = R′ = H

Dibenzo-α-pyrones are obtained in particularly good yield with peroxides **1d** and **1e**. On the contrary, dibenzoyl peroxides without electron-releasing meta substituents (i.e. **1a**, **1f**, and **1g**) give mainly ortho-benzoyloxylation phenols **4** with formation of **7** in very low yield, if any (Table I, entries 1, 2, 9, and 10). Both **7** and **4** were completely absent in the reactions of diaroyl peroxides with hydroquinone (**2f**) in several solvents. In the last case, 1,4-benzoquinone and the corresponding benzoic acid were obtained in nearly quantitative yield (see the Experimental Section). The formation of **7** is not related to the use of phenols as solvents, even if their yield is maximized under these conditions. In Table II are summarized the product distribution in the decomposition of **1a**, **1c**, and **1d** in the

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Table II. Product Distribution in the Decomposition of Diaroyl Peroxides (1a, 1c, and 1d) in the Presence of 4-Methylphenol (2b) in Different Solvents (1.5 M, 60 °C)

			products (relative yields, %)				
entry	1	solvent	3	4	6	7	8
1	1a	chloroform[a]	3.1	80.3	16.5	–	–
2	1a	benzene[b]	2.4	77.3	20.3	–	–
3	1a	hexane[c]	2.0	91.8	6.2	–	–
4	1a	hexane + Nujol[d]	1.8	98.5	1.4	–	–
5	1a	Nujol[e]	<1	99.2	0.7	–	–
6	1c	benzene[b]	16.1	67.8	–	16.1	–
7	1c	Nujol[e]	8.6	46.8	–	41.3	–
8	1d	benzene[b]	10.3	70.3	–	19.4	–
9	1d	Nujol[e]	6.4	25.7	–	67.9	–

[a] Polarity index (π) and viscosity: 4.4 and 0.39. [b] 3 and 0.39. [c] 0.06 and 0.21. [d] 0.06 and 2 (determined by the Kendall equation). [e] 0.06 and 4.2 (deduced by interpolation of literature data[21]).

Table III. Products Distribution in the Decomposition of Dibenzoyl Peroxide (1a) in the Presence of 4-Methylphenol (2b) in Benzene at 60 °C

molar ratio		products (relative yields, %)		
1a and 2b	benzene	3	4	6
0.125	0.75	2.4	77.3	20.3
0.20	0.60	2.8	82.3	14.9
0.33	0.33	2.9	87.8	9.7
0.40	0.20	3.0	88.9	8.1
0.44	0.11	3.0	90.1	6.9
0.5	–	13.5	81.6	4.8

presence of **2b** in various solvents.

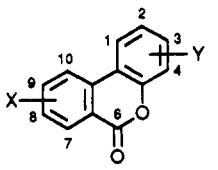
The kinetics of the reaction between **1c** and **2b** was followed in 0.1 M benzene solution at 30 °C by infrared spectroscopy (see the Experimental Section). The reaction was cleanly first-order in phenol and peroxide, in close analogy with other reaction of this class,[2] and a mean value of 1.37×10^{-5} M^{-1} s^{-1} for the rate constant was deduced. A similar value has been reported[3] in the same solvent at 30 °C for the decomposition of **1a** with **2b** (1.07×10^{-5} M^{-1} s^{-1}) in which **7** is completely absent.

Products of C–C homocoupling of phenol **2** (i.e. **3a** or **3b**) were generally observed in these reactions, when either **7** or **4** were formed as major products. They correspond to an ortho–ortho C–C coupling process and neither products of ortho–para, para–para or O–C coupling were detected, in sharp contrast with typical results of oxidation of 4-methylphenol occurring through dimerization of phenoxy radical intermediates.[11] The yield of **3** was found to linearly decrease in all solvents decreasing the concentration of the phenol (Table III).

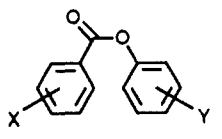
Also the viscosity of the solvent plays a significant role in the product distribution. For instance, the diphenol **3** and the 4-(benzoyloxy)-4-methylcyclohexadienone (**6ab**) were formed in lower yield when **1a** was decomposed in the presence of **2b** in solvents of low polarity or higher viscosity (Table II). Moreover, a similar trend was observed for compound **4** in reactions where compound **7** was also formed, so that an higher selectivity for **7** can be reached in Nujol as solvent.

The compound **6ab**, generally observed in the decomposition of **1a** in the presence of **2b** in various solvents and at different concentrations of reagents (Table III) is stable under the reaction conditions and does not rearrange to the *o*-benzoyloxy derivative **4ab**.

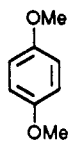
The decomposition of bis(3,5-dimethoxybenzoyl) peroxide (**1c**) at 60 °C in neat 1,4-dimethoxybenzene (**9**) or in 0.1 M benzene solution affords the ortho-benzoyloxylated product **10c** in 82 and 70% yield, respectively, without formation of products of homo- or heterocoupling. These results follows the general trend observed in the decomposition of dibenzoyl peroxide and polyoxy-substituted benzenes.[3]



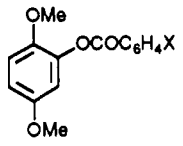
7aa: X = H; Y = H
ab: X = H; Y = 2-Me
ae: X = H; Y = 2-OMe
bb: X = 8-OMe; Y = 2-Me
cb: X = 8,10-(OMe)$_2$; Y = 2-Me
db: X = 8,9-(OMe)$_2$; Y = 2-Me
eb: X = 8,9,10-(OMe)$_3$; Y = 2-Me
dc: X = 8,10-(OMe)$_2$; Y = 3-Me
cb: X = 8,10-(OMe)$_2$; Y = 1-Me,3-OH
7'bb: X = 10-OMe; Y = 2-Me



8aa: X = H; Y = H
bb: X = 3-OMe; Y = 4-Me
cb: X = 3,5-(OMe)$_2$; Y = 4-Me
db: X = 3,4-(OMe)$_2$; Y = 4-Me
eb: X = 3,4,5-(OMe)$_3$; Y = 4-Me
dc: X = 3,4-(OMe)$_2$; Y = 3-Me
dd: X = 3,4-(OMe)$_2$; Y = 3-OH, 5-Me



9



10a: X = H
c: X = 3,5-(OMe)$_2$

The benzoic esters of phenols **8** were commonly obtained as side products in several of these reactions. In order to determine if they were intermediates in the formation of pyrones **7**, several attempts were made to oxidize them by monoelectronic metal oxidants (i.e. $Mn(OAc)_3$, $Ce(NH)_4(NO)_6$, $Tl(NO)_3$, VOF_3) or by bis(substituted benzoyl) peroxides. In all cases **7** was absent from the reaction mixtures. Compounds **8** arises from transesterification processes of the initially obtained **4** with phenol in excess, because their yield parallel the reactivity of **4** toward nucleophiles.

Finally, the oxidation of the diphenol **2g** in benzene by the peroxide **1c** allowed us to isolate in high yield a yet unidentified polymeric material without traces of the corresponding ortho-benzoyloxylation product or pyrone. Products of arylation of the phenols were detected only when the decomposition temperature was higher than 60 °C.

Concerning the mechanism of the formation of **7**, all the results obtained in experiments with bis(3-methoxy-substituted benzoyl) peroxides does not support an electrophilic mechanism,[3] because the electrophilic oxygen atom is clearly not involved. On the other hand, compounds **3** and **7** are formed competitively with the more usual ortho-benzoyloxylation product **4**, as can be also deduced from the kinetic data. Conversely, the formation of biaryl by C–C coupling are among the most important reactions

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of the aromatic radical cations, which can occur through two different mechanism referred as radical–radical (RRD) and radical–substrate (RSD) dimerization.[12] The RSD process is generally reported to be fast, reversible, and able to compete successfully with the addition to charged nucleophiles. We therefore suggest that pyrones **7** and diphenol **3** are formed through addition of phenol radicals cations, formed in the interaction between the diaroyl peroxide and the phenol to the aromatic ring of the benzoate anion or to other phenol molecules of the cage by C–C and C–O coupling, respectively. The postulated intermediates 2′-hydroxybiphenylcarboxylic acids are known[13] to cyclize efficiently in acid medium to pyrones **7**.

Our experiments show how essential a high electron density of the aromatic ring for the C–C biaryl bond formation is and, in any case, that free radicals do not escape from the solvent cage.

The RSD mechanism for the formation of biphenols **3** is supported by the observation that **3b** was the only biphenol detected (a result never observed before in the oxidation of **2b** with metal or peroxide oxidants[11]) and that its yield depends upon the concentration of starting phenol, either when **7** was formed or not (Tables II and III, respectively). The competition between the formation of pyrones **7** and *o*-(benzoyloxy)phenol **4** can be rationalized on the basis of the known reactivity of the radical cation toward charged and uncharged highly polarizable nucleophiles, and experiments in increasing viscosity media indicate that different ionic reactivity of radical ion pairs is probably related to minor modifications of the mobility of partners within the solvent cage.

The observation that the heterocoupling processes are not observed with 1,4-dimethoxy- and 1,4-dihydroxybenzene can be rationalized with the lower reactivity of the corresponding radical cations. In fact, the first substrate dimerizes and polymerizes slowly when submitted to monoelectronic oxidation,[14] and the radical cation of the hydroquinone deprotonates quite efficiently.

Experimental Section

Melting points were determined on a Thomas hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 467 spectrometer. Kinetic data were obtained on a Perkin Elmer 781 spectrometer using cuvettes of 1 cm path length at 30 °C. ^{1}H NMR spectra were obtained on a Varian AM 90 or Bruker AC 200 spectrometer, with $CDCl_3$ as solvent and tetramethylsilane as internal standard. Low-resolution mass spectra (MS) were recorded on either a Hitachi RMU-6 or a VG Micromax ZAB spectrometer, using the direct insertion probe.

HPLC analyses were carried out on a JASCO Twincle HPLC, equipped with a UV detector (254 nm) and a chromatographic data system under the conditions: reverse phase C-18 (2.5 × 100 mm) JASCO column (7 μm particles); mobile phase acetonitrile–water (4:1); flow rate 1 mL/min at 20 °C. Gas chromatographic analyses were performed on a Carlo Erba 4200 gas chromatograph, equipped with flame ionization detector and glass columns (2 m × 4 mm) packed with 10% OV 101 or 10% Carbowaks 20 M on Chromosorb W. Thin-layer chromatography (TLC) was performed on aluminum-backed Merck silica gel 60 F254 plates. Separations by flash chromatography were achieved with Merck silica gel (230–400 mesh) under a pressure of 0.4 atm.

Materials. Phenols (99% pure) were distilled under N_2 and soon used. 1,2-Bis(3-hydroxyphenyl)ethane (mp 139–140 °C)[15] and diphenol **3b** (mp 153–4 °C)[5] were synthesized according to the reported procedures. Compound **7aa** (mp 92–93 °C) was obtained from biphenyl-2-carboxylic acid, hydrogen peroxide, and trifluoroacetic acid.[16] Compounds **7cb** (mp 165–6 °C), **7eb** (mp 135 °C), **7ab** (mp 134–5 °C)[13] and **7ae** (mp 123–4 °C)[16] were independently synthesized in 20–30% yield by condensation of the appropriately substituted phenols and 2-bromobenzoic acids.[17] Diaroyl peroxides (**1**) were synthesized from the corresponding aroyl chloride, hydrogen peroxide, and pyridine[18] or from the acid, ethereal H_2O_2, and dicyclohexylcarbodiimide,[19] recrystallized from chloroform–methanol, and their purity was determined by iodimetry (acetic acid, 50 °C, 30 min). They present the following melting points (°C): **1a** (106–7 dec), **1b** (83–4), **1c** (144), **1d** (133), **1e** (138 dec), **1f** (128 dec), **1g** (157–8 dec).[20] All the esters **8** were obtained by dicyclohexylcarbodiimide condensation from the corresponding benzoic acid and phenols.

General Procedure for the Decomposition of 1a–f in Neat Phenols. The phenol (10 g) was introduced in a flash and heated under N_2 at 30–60 °C until fusion ensured. Magnetic stirring was started and the diaryl peroxide (5.0 mmol) was introduced in 5 min. The resulting solution was kept for 3 h in a thermostatic bath, following the decomposition of peroxide by TLC. The phenol in excess was distilled of at 60 °C under vacuum, and the resulting residue was column chromatographed using mixtures of hexane–ethyl acetate (90:10 to 0:100) as eluent. In a parallel run, the reaction mixture was cooled, a sample (0.2 g) was withdrawn, dissolved in acetonitrile containing a weighed amount of ippuric acid as internal standard, and analyzed by HPLC for quantitative determinations. The results are reported in Table I.

From the preparative runs compounds **3**, **4**, **6**, **7**, and **8** were isolated and identified, when known, by comparison with IR, NMR spectra, and GLC and HPLC retention times of authentic samples.

The new pyrons show the following analytical data.

7bb: mp 123 °C; IR (cm^{-1}) 1720; ^{1}H NMR ($CDCl_3$) δ 2.4 (s, 3 H, Me), 3.9 (s, 3 H, OMe), 7.2 (m, 2 H, $H_{3,4}$), 7.3 (dd, 1 H, H_9, J = 8 Hz, J = 3 Hz), 7.75 (s, 1 H, H_1), 7.8 (d, 1 H, H_7, J = 3 Hz), 8.0 (d, 1 H, H_9, J = 8 Hz); MS m/e 240 ($M^{\bullet+}$, 100), 225 (44), 197 (12), 195 (12), 169 (28), 141 (10), 139 (12), 115 (16). Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.14; H, 5.09.

7′bb: IR (cm^{-1}) 1710; ^{1}H NMR ($CDCl_3$) δ 2.5 (s, 3 H, Me), 4.1 (s, 3 H, OMe), 6.9 (dd, 1 H, H_9, J = 7 Hz, J = 2.5 Hz), 7.2 (m, 2 H, $H_{3,4}$), 7.5 (t, 1 H, H_8, J = 7 Hz), 8.15 (dd, 1 H, H_7, J = 7 Hz, J = 2.5 Hz), 8.8 (s, 1 H, H_1); MS m/e 240 ($M^{\bullet+}$, $C_{15}H_{12}O_3$, 100), 225 (39), 169 (10), 141 (15), 115 (11).

7cb: mp 166 °C; IR (cm^{-1}) 1710; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3 H, Me), 3.92 (s, 3H, OMe), 4.02 (s, 3 H, OMe), 6.87 (d, 1 H, H_9, J = 2.7 Hz), 7.19 and 7.22 (AB system, 2 H, $H_{3,4}$, J = 8.4 Hz), 7.51 (dd, 1 H, H_7, J = 2.7 Hz), 8.7 (s, 1 H, H_1); MS m/e 270 ($M^{\bullet+}$, 100), 255 (33), 228 (22), 213 (14), 185 (12), 135 (M^{2+}, 11). Anal. Calcd for $C_{15}H_{12}O_4$: C, 71.10; H, 5.22. Found: C, 70.92; H, 5.31.

7db: mp 219 °C; IR (cm^{-1}) 1710; ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H, Me), 3.98 and 4.09 (s, 3 H, OMe), 7.25 (s, 2 H, $H_{3,4}$), 7.42 (s, 1 H, H_{10}), 7.80 (m, 1 H, H_1), 7.85 (s, 1 H, H_7); MS m/e 270 ($M^{\bullet+}$, 100), 255 (24), 227 (12), 225 (12), 214 (21), 199 (12), 165 (26), 155 (16). Anal. Calcd for $C_{15}H_{12}O_4$: C, 71.10; H, 5.22. Found: C, 71.50; H, 5.11.

7eb: mp 135 °C; IR (cm^{-1}) 1720; ^{1}H NMR ($CDCl_3$) δ 2.5 (s, 3 H, Me), 3.98 (s, 6 H, OMe), 4.03 (s, 3 H, OME), 7.25 (m, 2 H, $H_{3,4}$), 7.83 (s, 1 H, H_7), 8.65 (m, 1 H, H_1); MS m/e 300 ($M^{\bullet+}$, 100), 285 (35), 270 (15), 242 (18), 199 (10), 171 (18), 150 (M^{2+}, 11), 115 (13). Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.99; H, 5.37. Found: C, 68.12; H, 5.52.

7dc: mp 222 °C; IR (cm^{-1}) 1710; ^{1}H NMR ($CDCl_3$) δ 2.5 (s, 3 H, Me), 4.0 and 4.1 (s, 3 H, OMe), 7.2 (m, 2 H, $H_{3,4}$), 7.8 (s, 1 H, H_{10}), 7.9 (s, 1 H, H_1), 7.95 (s, 1 H, H_7); MS m/e 270 ($M^{\bullet+}$, 100), 255 (19), 227 (10), 225 (11), 214 (20), 199 (17), 184 (9), 135 (M^{2+},

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Table IV. Decomposition of 0.01 M Benzene Solutions of 1c in the Presence of 2b at Various Concentrations

[2b], M	k (M^{-1} s^{-1} × 10^5)
0.05	1.31
0.10	1.40
0.15	1.38
0.20	1.36

10). Anal. Calcd for $C_{15}H_{12}O_4$: C, 71.10; H, 5.22. Found: C, 72.24; H, 5.32.

7cd: mp 182 °C; IR (cm^{-1}) 3200, 1735; ^1H NMR ($CDCl_3$) δ 2.36 (s, 3 H, Me), 3.95 and 4.09 (s, 3 H, OMe), 6.73 (m, 1 H, H_4), 6.77 (m, 1 H, H_2), 7.00 (d, 1 H, H_9, J = 2.6 Hz), 7.69 (d, 1 H, H_7), 9.4 (braod, 1 H, OH); MS m/e 286 ($M^{\bullet+}$, 100), 271 (27), 244 (19), 239 (6), 216 (8), 143 (M^{2+}, 10). Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.12; H, 4.93. Found: C, 67.40; H, 5.02.

6ab: mp 76 °C; IR (cm^{-1}) 1710, 1670; ^1H NMR ($CDCl_3$) δ 1.6 (s, 3 H, Me), 6.3 (d, 2 H, $H_{2,6}$, J = 10 Hz), 7.0 (d, 2 H, $H_{3,5}$, J = 10 Hz), 7.3–8.1 (m, 5 H, Ph); MS m/e 228 ($M^{\bullet+}$, $C_{14}H_{12}O_3$, 1), 107 (24), 105 (100), 77 (38).

Effect of Solvent and Temperature on the Reaction between 1a, 1c, or 1d and 2b. p-Cresol (**2b**, 1.08 g, 10 mmol) was mixed under N_2 with the solvents and at the concentrations reported in Tables II and III. The resulting solution was heated at 60 °C, and the peroxide **1a** (or **1c**, **1d**) (10 mmol) was added once. The reaction was kept at 60 ± 0.5 °C for 6–12 h, cooled at room temperature, and analyzed by HPLC as described before. The results obtained are reported in Tables II and III.

Kinetic Experiments. The kinetics for the decomposition of the peroxide **1c** were carried out under N_2 in 0.01 M benzene solutions in the presence of 0.05–0.2 M concentration of **2b** at 30 °C in a thermostated infrared cell, following the decrease with time of the carbonyl stretching of the peroxide at 1770 cm^{-1}. The data give good first-order plot, and the order in respect to the phenol was determined by varying its initial concentration. Table IV shows the data obtained.

Reaction between 1c and 1,4-Dimethoxybenzene. The peroxide **1c** (1 g, 2.76 mmol) was added once to 1,4-dimethoxybenzene (10 g, 72.5 mmol) heated at 60 °C under N_2 and vigorously stirred. The reaction was run for 6 h at 60 °C. Then 1,4-dimethoxybenzene was distilled off at the same temperature under N_2, and the residue was chromatographed on silica gel with 8:2 hexane–ethyl acetate as eluent. After minor impurities, **10c** was separated as white needles (0.74 g, 85%): mp 87–88 °C (from pentane–diethyl ether); MS m/e 318 ($M^{\bullet+}$, 26), 165 (100), 137 (13), 107 (5); ^1H NMR ($CDCl_3$) δ 7.36 (d, 2 H, J = 2.6 Hz), 6.94 (d, 1 H, J = 9.1 Hz), 6.79 (d, 1 H), 6.78 (m, 1 H), 6.76 (d, 1 H), 6.71 (t, 1 H), 3.85 (s, 6 H, OMe), 3.78 (s, 6 H, OMe). Anal. Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 64.37; H, 5.91.

Reaction between 1a–e and Hydroquinone. Hydroquinone (0.55 g, 5 mmol) was dissolved in chloroform (10 mL), and the solution heated at 60 °C and vigorously stirred. The peroxide (**1a–e**, 5 mmol) was added in 5 min as solid, and the reaction was stirred for 2 h. The analysis of the reaction mixture was carried out directly by GLC using the 10% Carbowaxs 20 M column at 110 °C. 1,4-Benzoquinone was found to be formed in 88, 72, 78, 82, and 80% yield with **1a**, **1b**, **1c**, **1d**, and **1e**, respectively. Acid–base separations of the final solution allows to obtain benzoic acid in 90–95% yield in all experiments.

Registry No. **1a**, 94-36-0; **1b**, 1712-86-3; **1c**, 129194-36-1; **1d**, 129194-37-2; **1e**, 129194-38-3; **1f**, 849-83-2; **1g**, 1712-84-1; **2a**, 108-95-2; **2b**, 106-44-5; **2c**, 108-39-4; **2d**, 504-15-4; **2e**, 150-76-5; **2f**, 123-31-9; **2g**, 70709-67-0; **3a**, 1806-29-7; **3b**, 15519-73-0; **3d**, 129194-54-3; **4aa**, 5876-92-6; **4ab**, 22932-58-7; **4bb**, 129194-39-4; **4cb**, 129194-40-7; **4db**, 129194-41-8; **4fb**, 129194-42-9; **4gb**, 129194-43-0; **6ab**, 92254-31-4; **7aa**, 2005-10-9; **7ab**, 58586-45-1; **7ae**, 3701-38-0; **7bb**, 129194-44-1; **7'bb**, 129194-45-2; **7cb**, 129194-46-3; **7cd**, 129194-47-4; **7db**, 129194-48-5; **7dc**, 129194-49-6; **7eb**, 129194-50-9; **8aa**, 93-99-2; **8ab**, 614-34-6; **8bb**, 73991-81-8; **8db**, 129194-51-0; **8eb**, 129194-52-1; **8fb**, 58600-95-6; **9**, 150-78-7; **10c**, 129194-53-2; 1,4-benzoquinone, 106-51-4; benzoic acid, 65-85-0.