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Electrochemical Synthesis and X-Ray Molecular Structure of 2-Arylimino-4,5-Diaryl-1,3-Dioxoles

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Abstract : *Selective cathodic reduction of diaryl-1,2-diketones in the presence of N-arylcarbonimidoyl dichlorides leads to 2-arylimino-4,5-diaryl-1,3-dioxoles, a little known class of heterocycle, in almost quantitative yields. NMR spectra of these compounds show a remarkable dependence upon temperature associated with a low configurational stability around the carbon-nitrogen double bond. An x-ray crystallographic analysis has been performed, showing an unusually short carbon-nitrogen double bond, which might be expected to be longer to explain the mechanism of the facile thermal isomerization through a polar transition state in which the double bond character is lost.*

The majority of papers concerning the electrochemical reduction of diaryl-1,2-diketones have been focused on benzil. Cathodic reductions under a variety of protic media have been studied, with the establishment of mechanism as the main purpose[1]. Overall the reactions correspond to two-electron, two-proton processes, with formation of stilbenediols that are later converted spontaneously into benzoins by enol-keto tautomerization. However, from a synthetic point of view, the cathodic reductions in aprotic media in the presence of non-electroactive electrophilic reagents are of great interest. Thus, the attack of electrogenerated intermediates on the electrophilic reagents can take place instead of simple protonation. Nevertheless, few investigations of this type of preparative electrolysis have been carried out. Acyl halides or carboxylic acid anhydrides and simple alkyl halides have been used as electrophiles[2-6] to obtain enediol diesters or ethers.

As was reported in a preliminary communication[7] we have found a new, simple and very efficient electrochemical iminocarbonylation process for diaryl-1,2-diketones. The 2-arylimino-4,5-diaryl-1,3-dioxoles **5** can be conveniently prepared by selective cathodic reduction of the diketones **1** in the presence of N-arylcarbonimidoyl dichlorides **3,** which are easily available from isothiocyanates, isocyanates and Nmonosubstituted formamides[8]. Carbonimidoyl dichlorides themselves undergo electrochemical reduction giving isocyanides[9] in almost quantitative yields. However, the reduction potentials of diaryl-1,2-diketones and carbonimidoyl dichlorides are different enough to allow a selective reduction of the diketones. Thus, both chlorine atoms of carbonimidoyl dichlorides are displaced by nucleophilic attack of negatively charged electrogenerated intermediates, closing the 1,3-dioxole heterocyclic ring.

In a literature survey it is apparent that chemistry related to different classes of 1,3-dioxoles has been studied over a long period[10]. However, the 2-imino derivatives have scarcely been investigated. This is perhaps because a convenient synthesis had not been reported prior to the present electrochemical procedure. The only previously reported method for preparing this type of dioxole compounds is reaction of bis(tributylstannyloxy)ethenes with isothiocyanates[11]. This method requires the prior synthesis of diethylaminotributylstannane by a complex and expensive procedure. Only two reaction examples were reported, with remarkably different yields.

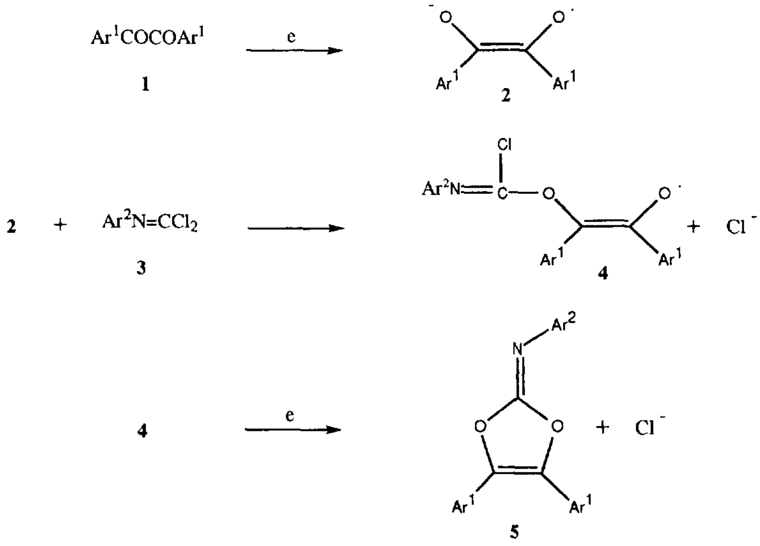
RESULTS AND DISCUSSION

Cathodic reductions of solutions of diaryl-1,2-diketones **1** in DMF-$LiClO_4$ at a mercury pool cathode, under constant potential were carried out in the presence of equimolecular amounts of carbonimidoyl dichlorides **3**. After a few seconds the colour of the catholyte solutions, initially yellow, turned to purple. When the current was interrupted the solutions became yellow again. This observation can be repeated throughout the electrolysis. The electricity consumption was 2 F/ mol of diketone. After electrolysis, crude solid reaction products were easily isolated by simple mixing of the catholyte solution with water. After crystallization the products were identified by IR, MS, high field NMR spectroscopy and microanalyses as the corresponding 2-arylmino-4,5-diaryl-1,3-dioxoles **5**. Yields were almost quantitative.

The results of spectroscopic structural analyses were in agreement with the results of acidic hydrolysis, which afforded the expected 4,5-diaryl-1,3-dioxol-2-ones **6** in high yields. Since products **6** are obtained avoiding the use of the extremely toxic phosgene as reagent[12], this hydrolytic reaction has a significant interest as an alternative method of preparation. The synthesis of product **5a** was previously reported through the organostannane method[11]. The rest of the entries correspond to new iminodioxoles and new dioxolenones.

The electrochemical reduction of 4-methoxybenzil was also studied. In contrast to the results of the above cathodic reductions of symmetrical benzils, materials with undefined physical properties were isolated. In these cases analyses indicated a nearly quantitative formation of a mixture of both E and Z iminocarbonates isomers **7** in a ratio of ca. 1:1. NMR spectroscopy demonstrates that isomers **7** undergo facile thermal interconversion. Attempts to separate them were unsuccessful.

Benzil was also reduced using 1,4-phenylene-bis(carbonimidoyl dichloride) as electrophilic reagent (ratio 2:1). The electrolysis afforded 2-(1,4-phenylenediimino)-bis(4,5-diphenyl-1,3-dioxole) **8**, a previously unknown compound, in almost quantitative yield.

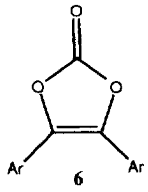


Scheme 1

Entry	Ar^1	Ar^2	Entry	Ar^1	Ar^2
5a	C_6H_5	C_6H_5	**5g**	4-MeO-C_6H_4	4-Cl-C_6H_4
5b	C_6H_5	4-Cl-C_6H_4	**5h**	4-MeO-C_6H_4	2,4-$Cl_2C_6H_3$
5c	C_6H_5	2-Cl-4-Me-C_6H_3	**5i**	4-Br-C_6H_4	2-Cl-4-Me-C_6H_3
5d	C_6H_5	2,4-$Cl_2C_6H_3$	**5j**	4-Br-C_6H_4	C_6H_5
5e	4-MeO-C_6H_4	C_6H_5	**5k**	4-Br-C_6H_4	4-Cl-C_6H_4
5f	4-MeO-C_6H_4	2-Cl-4-Me-C_6H_3	**5l**	2-MeO-C_6H_4	4-Cl-C_6H_4

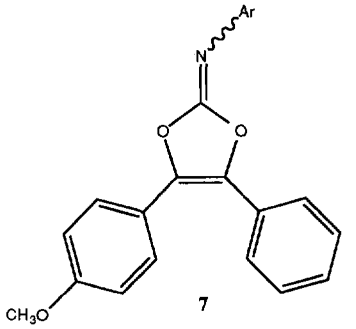
The formation of aryliminodioxoles can be rationalized through a reaction route as outlined in Scheme 1. The participation of semidione radical anions **2** has been evidenced in different electroreductive studies of a-diketones[2,4,13,14] and has been demonstrated by electron spin resonance spectroscopy[15]. Benzil radical anion has been generated by reduction with alkali metals[16], showing a purple color. Induction from the negative polarity of the cathode surface[2,4] and a higher stability of Z semidione radical anions than the E isomers have both been postulated as crucial factors in determining the stereoselective formation of Z products. In spite of the coulombic and steric repulsions, a higher stability of Z semidione radical anions is attributed to a more efficient coordination with metal cations of the electrolyte[16].

The transient purple colour observed during the electrolysis indicates that intermediates **2** are relatively long-lived in the catholyte. In contrast, this colour is not observed when electroreduction of diketones **1** is carried out in the presence of acyl chlorides or carboxylic acid anhydrides. In this case the same intermediates are shorter-lived because of the greater electrophilic character of the reagents.



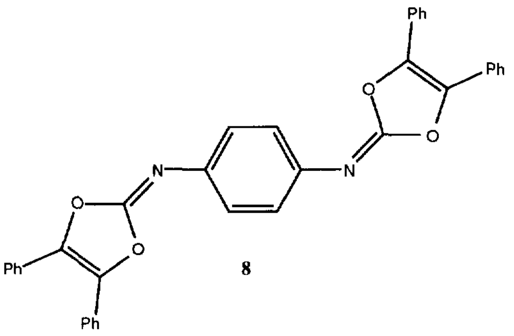
6

Entry	Ar
6a	4-MeO-C_6H_4
6b	4-Br-C_6H_4
6c	2-MeO-C_6H_4



7

Entry	Ar
7a	C_6H_5
7b	4-Cl-C_6H_4



8

An interesting feature of the reaction mechanism was observed on carrying out a non-exhaustive cathodic reduction of benzil in the absence of carbonimidoyl dichloride. This reaction gave a strongly coloured purple solution. After interrupting the current N-phenylcarbonimidoyl dichoride was added, which caused a rapid discoloration of the catholyte solution. The formation of a significant amount of 4,5-diphenyl-2-phenylimino-1,3-dioxole **5a** was detected by gas chromatography-mass spectrometry analysis. This experiment must be considered as firm evidence for the participation of semidione radical anion **2** as an indirect electron transfer agent in the reduction process. Therefore, both a direct electron transfer from the cathode and an indirect one from intermediates **2**, in homogeneous medium, are plausibly involved in the second electron transfer step.

NMR spectra of synthesized iminodioxoles, especially ^{13}C NMR spectra, show a remarkable dependence upon temperature. Assignment of spectra have been made by DEPT; H,C-COSY; and Selective Decoupling techniques. The carbon atoms of the aryl groups attached to nitrogen are denoted as 1"-4" or 1-6" depending on symmetry, whereas 1,2, ... and 1',2', ... correspond to the aryl groups attached to the carbons of the dioxole ring. A similar notation is used for products **7**, the carbon atoms of the methoxyphenyl groups being denoted as 1'-4'. Some unusually broad peaks were observed in ^{13}C NMR spectra with the sample at ambient temperature. Generally the number of resonance signals was lower than expected, taking the double bonded carbon atoms of dioxole ring as well as the 1,1'; 2,2'; ... carbon pairs as non-equivalent nuclei, but higher than predicted for complete equivalence. However, through a moderate increase of the temperature all peaks became sharp and the number was reduced to that expected for equivalent nuclei. Spectra at low temperature were also recorded. All peak were sharp and the number increased to almost that predicted for non-equivalent carbon pairs. In these experiments it was clearly shown that the simplest spectra become progressively more complex by an unfolding of the peaks corresponding to the above noted pairs of carbon atoms. It is notable that an unfolding of signals of carbons 3,3' was not observed in any case. Results of the same nature were obtained for products **7**. The spectra were very complex, in this case due to the presence of both Z and E isomers.

These spectroscopic phenomena must be attributed to a relatively low configurational stability around the carbon-nitrogen double bond. Either rotation or inversion mechanisms have been postulated to explain syn-anti isomerization of compounds containing carbon-nitrogen double bonds[17]. The rotation mechanism implies a polar transition state involving loss of the carbon-nitrogen double bond character. Inversion is the other, opposite mechanism and implies rehybridization of the non-bonded electron pair on nitrogen to a p orbital, with the carbon-nitrogen double bond character remaining unaffected.

Geometrical characteristics of this class of compounds were determined by X-ray crystallography of compound **5c**. The molecular structure found is illustrated in Figure 1. The heterocyclic dioxole ring shown is an almost regular pentagon. Selected intramolecular distances (crystallographic numbering of atoms) and selected bond angles are given in Table 1. The main noteworthy feature of this structure is the unusually short carbon-nitrogen double bond (1.254(2) Å, (cf. standard[18] C(sp^2) - C=N-C bond length of 1.279 Å). However, this bond might be expected to be longer to explain the mechanism of the observed facile thermal isomerization through a polar transition state in which the double bond character of the C3-N bond is lost.

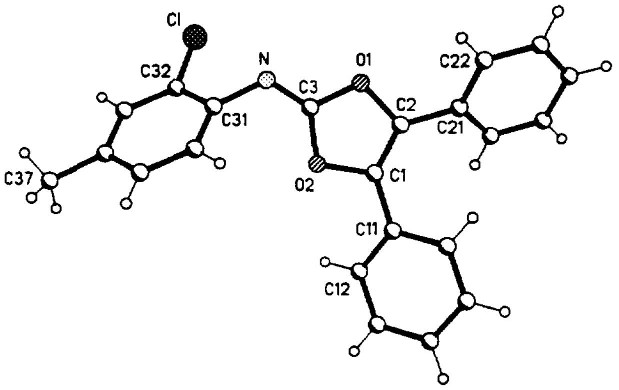


Figure 1. Molecular structure of **5c**, *showing the crystallographic numbering system used.*

Table 1. Selected Bond Lengths and Bond Angles in Crystal Structure of **5c**

Bond lenghts (Å)

C(1)-C(2)	1.329(2)	C(1)-O(2)	1.409(2)
C(1)-C(11)	1.459(2)	C(2)-O(1)	1.400(2)
C(2)-C(21)	1.461(2)	C(3)-N	1.254(2)
C(3)-O(1)	1.353(2)	C(3)-O(2)	1.362(2)
C(31)-N	1.411(2)	C(34)-C(37)	1.508(3)
C(32)-Cl	1.732(2)		

Bond angles (°)

C(2)-C(1)-O(2)	108.2(2)	C(2)-C(1)-C(11)	134.7(2)
O(2)-C(1)-C(11)	116.94(14)	C(1)-C(2)-O(1)	108.7(2)
C(1)-C(2)-C(21)	134.8(2)	O(1)-C(2)-C(21)	116.5(2)
N-C(3)-O(1)	121.3(2)	N-C(3)-O(2)	129.1(2)
O(1)-C(3)-O(2)	109.60(14)	C(16)-C(11)-C(1)	119.4(2)
C(26)-C(21)-C(2)	120.0(2)	C(22)-C(21)-C(2)	120.5(2)
C(36)-C(31)-N	124.3(2)	C(32)-C(31)-N	118.6(2)
C(3)-O(1)-C(2)	106.90(13)	C(3)-N-C(31)	121.0(2)
C(3)-O(2)-C(1)	106.50(13)		

EXPERIMENTAL

NMR spectra were determined on Bruker AC-200 or Varian AC-300 Unity instruments with tetramethylsilane as internal reference. Electron-impact mass spectra were obtained on a Hewlett-Packard 5995 spectrometer with direct insertion probe and an ionizing voltage of 70 eV. IR spectra (Nujol emulsions) were recorded on a Nicolet-5DX spectrophotometer. Microanalyses were performed on a Carlo Erba EA-1108 analyzer. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected.

Electrochemical experiments were performed with an Amel 557 potentiostat coupled to an Amel 558 integrator.

X-Ray Crystallographic Analysis of 5c. *Crystal data:* $C_{22}H_{16}ClNO_2$, Mr = 361.81, monoclinic, C2/c, a = 29.260 (6), b = 7.396 (2), c = 18.843 (4) Å, β = 121.638 (14) °, V = 3471.7 Å^3, Z = 8, λ (Mo Kα) = 0.71073 Å, T = -130°C. *Data collection:* Colourless prism 0.9 x 0.3 x 0.3 mm, Stoe STADI-4 diffractometer, 4068 intensities (3992 unique), $2\theta_{max}$ 55°. *Structure solution and refinement:* Direct methods, refined on F^2 (program SHELXL-93, G.M. Sheldrick, University of Göttingen), H atoms with riding model, wR (F^2) 0.111, R (F) 0.045, 237 parameters, S = 1.08, max. $\Delta\rho$ 0.30 e Å^{-3}.

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CDS - 400954.

Materials

Diaryl-1,2-diketones were obtained from comercial sources and were used as received except for 2,2'-dimethoxybenzil which was prepared by a standard procedure[19]. Carbonimidoyl dichlorides were also prepared by standard procedures[8]. DMF was taken from a freshly opened bottle and dried with molecular sieve. $LiClO_4$ was anhydrous. Both were purchased from Fluka, and were used directly without purification.

Electrolysis Procedure

Preparative electrolyses were performed under a constant cathodic potential in a concentric cylindrical cell with two compartments separated by a circular glass frit (medium) diaphragm. A mercury pool (diameter 5 cm) was used as the cathode and a platinum plate as the anode. The catholyte was magnetically stirred. The temperature was kept at approximately 18 °C by external cooling. The reductions were carried out in DMF-$LiClO_4$, 0.2 M. Approximately 35 mL and 15 mL of this solution were placed in the cathodic and the anodic compartments, respectively. To prevent accumulation of electrogenerated acid in the anode compartment, anhydrous sodium carbonate (3 g) was placed in this compartment. Solutions of diaryl-1,2-diketones **1** (5 mmol) and carbonimidoyl dichlorides **3** (5 mmol) were electrolyzed under the following cathodic potentials: -0.95 V vs SCE (entries **5b**, **5g**, **5k**,); -1.00 V (entries **5a**, **5d**, **5e**, **5h**, **5j**, **5l**); -1.05 V (entries **5c**, **5f**, **5i**). The electricity consumption was 2 F . mol^{-1} for all cases. Products **7** were obtained similarly by reduction of 4-methoxybenzil in the presence of phenylcarbonimidoyl dichloride (-1.00 V) or 2-chloro-4-

methylphenylcarbonimidoyl dichloride (-0.95 V). Cathodic reduction of benzil (5 mmol) in the presence of 1,4-phenylene-bis(carbonimidoyl dichloride) (2.5 mmol) (-0.95 V) gave product **8**. All electrolysis products were isolated in high purity state[20] by dropping the catholyte solution onto cold brine (200 mL) and filtrating or extracting the mixture with ether[21]. The ether layers were washed with cold water and dried on anhydrous sodium sulphate. The directly collected solid crude products and that obtained after removing ether under reduced pressure were isolated in nearly quantitative yields and were crystallized from acetonitrile[22].

4,5-diphenyl-2-phenylimino-1,3-dioxole (**5a**)

(91%), white prisms mp 177-178 °C. (Found: C, 80.38; H, 4.80; N, 4.43. $C_{21}H_{15}NO_2$ requires: C, 80.49; H, 4.82; N, 4.47); i.r. (Nujol): 1738, 1595, 1449, 1231, 1067, 1024, 956, 943, 791, 774, 760, 744, 694 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$, 200 MHz): 7.10 (m, 1H, H-4''), 7.29-7.42 (m, 10H, H-2'',3'',3,3',4,4'), 7.50-7.65 (br m, 4H, H-2,2'); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 123.33 (C-2''), 123.85 (C-4''), 125.85, 125.92 (br, C-1,1'), 126.47, 126.61, (br, C-2,2'), 128.93 (C-3''), 128.95 (C-3,3'), 129.85 (C-4,4'), 136.35, 136.77 (br, O-C=C-O), 143.00 (C-1''), 150.19 (C=N-); m.s., m/z (%): 313 (M^+, 1), 166 (51), 165 (100), 119 (27), 105 (37), 91 (35), 77 (62), 63 (31), 51 (43).

2-(4-chlorophenylimino)-4,5-diphenyl-1,3-dioxole (**5b**)

(95%), pale yellow plates mp 151-152 °C. (Found: C, 72.35; H, 4.06; N, 4.10. $C_{21}H_{14}ClNO_2$ requires: C, 72.52; H, 4.06; N, 4.03); i.r. (Nujol): 1744, 1667, 1493, 1451 1233, 1069, 959, 839, 779, 760, 694 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$, 300 MHz): 7.23 (d, 2H, J = 9.2 Hz, H-2''), 7.28 (d, 2H, J = 9.1 Hz, H-3''), 7.38-7.43 (m, 6H, H-3,3',4,4'), [7.55 (br m, 2H), 7.61(br m, 2H) H-2,2')]; ^{13}C n.m.r. δ (DMSO-d_6, 75.4 MHz, 100 °C): 124.61 (C-2''), 125.36 (C-1,1'), 126.54 (C-2,2'), 127.59 (C-4''), 128.78 (C-3''), 129.08 (C-3,3'), 130.06 (C-4,4'), 136.31 (O-C=C-O), 143.24 (C-1''), 149.87 (C=N-); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz, - 55 °C): 124.22 (C-2''), 124.80, 124.96 (C-1,1'), 125.63, 125.91 (C-2,2'), 128.28 (C-4''), 128.55 (C-3,3') 128.60 (C-3''), 129.52, 129.60 (C-4,4'), 135.71, 136.17 (O-C=C-O), 141.63 (C-1''), 150.31 (C=N-); m.s., m/z (%): 347 (M^+, 2), 166 (43), 165 (100), 125 (14), 105 (21), 90 (15), 89 (13), 77 (36), 63 (27), 51 (31).

2-(2-chloro-4-methylphenylimino)-4,5-diphenyl-1,3-dioxole (**5c**)

(92%), white prisms mp 185-186 °C. (Found: C, 72.96; H, 4.45; N, 3.91. $C_{22}H_{16}ClNO_2$ requires: C, 73.03; H, 4.46; N, 3.87); i.r. (Nujol): 1732, 1675, 1495, 1451, 1244, 1227, 1074, 1055, 1026, 959, 941, 882, 824, 775, 760, 692 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$, 300 MHz): 2.31 (s, 3H, CH_3), 7.03 (dd, 1H, J = 8.4 Hz, J = 1.5 Hz, H-5''), 7.18 (d, 1H, J = 8.2 Hz, H-6''), 7.24 (d, 1H, J = 1.5 Hz, H-3''), 7.34-7.42 (m, 6H, H-3,3',4,4'), [7.53 (br s, 2H), 7.60 (br s, 2H) H-2,2']; ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 20.60 (CH_3), 123.39 (C-6''), 125.71 (C-

1,1'), 126.47, 126.49 (br, C-2,2'), 127.28 (C-2"), 127.87 (C-5"), 128.82 (C-3,3'), 129.80 (C-4,4'), 130.16 (C-3"), 134.35 (C-4"), 136.71 (br, O-C=C-O), 139.16 (C-1"), 150.69 (C=N-); m.s., m/z (%): 361 (M^+, 1), 166 (52), 165 (100), 132 (20), 105 (24), 77 (45), 63 (19), 51 (34).

2-(2,4-dichlorophenylimino)-4,5-diphenyl-1,3-dioxole (**5d**)

(89%), pale yellow needles mp 158-159 °C. (Found: C, 65.82; H, 3.41; N, 3.69. $C_{21}H_{13}Cl_2NO_2$ requires: C, 65.99; H, 3.43; N, 3.66); i.r. (Nujol): 1731, 1673, 1475, 1450, 1241, 1231, 1072, 1051, 1025, 959, 942, 771, 692 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$, 200 MHz): 7.20-7.21 (m, 2H, H-5",6"), 7.37-7.42 (m, 7H, H-3,3',3",4,4'), 7.56 (br s, 4H, H-2,2'); ^{13}C n.m.r. δ ($CDCl_3$, 50.3 MHz): 124.55 (C-6"), 125.54 (C-1,1'), 126.55 (C-2,2'), 127.43 (C-5"), 128.57 (C-2"), 128.96 (C-3,3',4"), 129.58 (C-3"), 130.04 (C-4,4'), 136.95 (O-C=C-O), 140.85 (C-1"), 151.12 (C=N-); m.s., m/z (%): 383 (M^+ + 2, 7), 381 (M^+, 12), 166 (53), 165 (100), 124 (12), 105 (16), 89 (10), 77 (33), 63 (13), 51 (17).

4,5-bis(4-methoxyphenyl)-2-phenylimino-1,3-dioxole (**5e**)

(85%), white needles mp 152-153 °C. (Found: C, 73.73; H, 5.16; N, 3.77. $C_{23}H_{19}NO_4$ requires: C, 73.98; H, 5.13; N, 3.75); i.r. (Nujol): 1725, 1674, 1593, 1520, 1256, 1223, 1177, 1071, 1024, 957, 941, 847, 831, 783, 696 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 3.81 (s, 6H, OCH_3), 6.90 (d, 4H, J = 8.7 Hz, H-3,3') 7.09 (m, 1H, H-4"), 7.28-7.36 (m, 4H, H-2",3"), [7.46 (d, 2H, J = 8.7 Hz), 7.52 (d, 2H, J = 8.7 Hz) H-2,2']; ^{13}C n.m.r. δ (DMSO-d_6, 75.4 MHz, 70 °C): 55.36 (OCH_3), 114.68 (C-3,3'), 117.73 (C-1,1'), 122.82 (C-2"), 123.31 (C-4"), 128.00 (C-2,2'), 128.81 (C-3"), 135.06 (O-C=C-O), 144.33 (C-1"), 149.55 (C=N-), 160.38 (C-4,4'); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz, -70 °C): 55.29 (OCH_3), 113.80 (C-3,3'), 117.59, 117.71 (C-1,1'), 123.10 (C-2"), 123.52 (C-4"), 127.61, 127.13 (C-2,2'), 128.78 (C-3"), 134.56, 135.00 (O-C=C-O), 143.37 (C-1"), 150.49 (C=N-), 159.54, 159.62 (C-4,4'); m.s., m/z (%): 373 (M^+, 2), 226 (35), 211 (73), 168 (29), 152 (38), 140 (41), 139 (46), 135 (100), 92 (54), 91 (93), 77 (73), 64 (65), 63 (41).

2-(2-chloro-4-methylphenylimino)-4,5-bis(4-methoxyphenyl)-1,3-dioxole (**5f**)

(83%), white needles mp 157-158 °C. (Found: C, 68.38; H, 4.77; N, 3.31. $C_{24}H_{20}ClNO_4$ requires: C, 68.33; H, 4.78; N, 3.32); i.r. (Nujol): 1738, 1674, 1607, 1524, 1494, 1303, 1260, 1240, 1177, 1073, 1029, 945, 841, 833, 820 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 2.30 (s, 3H, CH_3), 3.82 (s, 6H, OCH_3), 6.89 (d, 4H, J = 8.1 Hz, H-3,3'), 7.02 (dd, 1H, J = 9.0 Hz, J = 1.8 Hz, H-5"), 7.18 (d, 1H, J = 8.1 Hz, H-6"), 7.23 (d, 1H, J = 1.8 Hz, H-3"), 7.38-7.58 (br m, 4H, H-2,2'); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 20.67 (CH_3), 55.40 (OCH_3), 114.36 (C-3,3'), 118.29 (C-1,1'), 123.52 (C-6"), 127.42 (C-2"), 127.92 (C-2,2'), 128.00 (C-5"), 130.21 (C-3"), 134.28 (C-4"), 135.74 (O-C=C-O), 139.43 (C-1"), 151.12 (C=N-), 160.53 (C-4,4'); m.s., m/z (%): 421 (M^+, 4), 226

(23), 211 (100), 183 (19), 168 (18), 152 (19), 135 (32), 132 (21), 77 (20).

2-(4-chlorophenylimino)-4,5-bis(4-methoxyphenyl)-1,3-dioxole (**5g**)

(90%), pale yellow needles mp 177-178 °C. (Found: C, 67.49; H, 4.44; N, 3.46. $C_{23}H_{18}ClNO_4$ requires: C, 67.73; H, 4.45; N, 3.43); i.r. (Nujol): 1732, 1667, 1520, 1491, 1306, 1258, 1232, 1179, 1067, 1024, 841, 831, 826 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$, 200 MHz): 3.83 (s, 6H, OCH_3), 6.91 (d, 4H, J = 8.8 Hz, H-3,3'), 7.23 (d, 2H, J = 8.9 Hz, H-2"), 7.27 (d, 2H, J = 8.9 Hz, H-3"), [7.47 (d, 2H, J = 8.8 Hz), 7.50 (d, 2H, J = 8.8 Hz) H-2,2']; ^{13}C n.m.r. δ ($CDCl_3$, 50.3 MHz): 55.40 (OCH_3), 114.41 (C-3,3'), 118.15, 118.25 (C-1,1'), 124.67 (C-2"), 127.86, 128.08 (C-2,2'), 128.72 (C-4"), 128.92 (C-3"), 135.40, 135.73 (O-C=C-O), 142.88 (C-1"), 150.85 (C=N-), 160.57 (C-4,4'); m.s., m/z (%): 407 (M^+, 3), 226 (19), 211 (100), 195 (14), 183 (19), 153 (37), 152 (27), 140 (24), 139 (26), 135 (51), 92 (27), 90 (25), 77 (40), 63 (25).

2-(2,4-dichlorophenylimino)-4,5-bis(4-methoxyphenyl)-1,3-dioxole (**5h**)

(88%), white needles mp 165-166 °C. (Found: C, 62.57; H, 3.85; N, 3.19. $C_{23}H_{17}Cl_2NO_4$ requires: C, 62.46; H, 3.87; N, 3.17); i.r. (Nujol): 1734, 1662, 1612, 1519, 1509, 1307, 1264, 1228, 1178, 1075, 1028, 824 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$, 200 MHz): 3.83 (s, 6H, OCH_3), 6.91 (d, 4H, J = 8.8 Hz, H-3,3'), 7.15-7.26 (m, 2H, H-5",6"), 7.41 (d, 1H, J = 1.6, H-3"), 7.46 (br s, 4H, H-2,2'); ^{13}C n.m.r. δ ($CDCl_3$, 50.3 MHz): 55.39 (OCH_3), 114.40 (C-3,3'), 117.99 (C-1,1'), 124.58 (C-6"), 127.38 (C-5"), 128.02 (br, C-2,2'), 128.60 (C-4"), 128.78 (C-2"), 129.52 (C-3"), 135.88 (O-C=C-O), 141.03 (C-1"), 151.47 (C=N-), 160.62 (C-4,4'); m.s., m/z (%): 443 (M^+ + 2, 56), 441(M^+, 76), 226 (100), 211 (79), 168 (23), 152 (26), 135 (42), 92 (20), 77 (25).

4,5-bis(4-bromophenyl)-2-(2-chloro-4-methylphenylimino)-1,3-dioxole (**5i**)

(84%), pale yellow needles mp 152-154 °C. (Found: C, 51.06; H, 2.69; N, 2.72. $C_{22}H_{14}Br_2ClNO_2$ requires: C, 50.85; H, 2.72; N, 2.70); i.r. (Nujol): 1722, 1665, 1497, 1237, 1219, 1076, 1049, 1008, 959, 943, 883, 829, 818 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$, 200 MHz): 2.30 (s, 3H, CH_3), 7.02 (dd, 1H, J = 8.1 Hz, J = 1.3 Hz, H-5"), 7.14 (d, 1H, J = 8.1, H-6"), 7.22 (d, 1H, J = 1.3 Hz, H-3"), 7.41 (br s, 4H, H-2,2'), 7.51 (d, 4H, J = 8.3 Hz, H-3,3'); ^{13}C n.m.r. δ ($CDCl_3$, 50.3 MHz): 20.67 (CH_3), 123.34 (C-6"), 124.32 (C-4,4'), 124.42 (C-1,1'), 127.25 (C-2"), 127.96 (C-2,2'), 128.00 (C-5"), 130.29 (C-3"), 132.33 (C-3,3'), 134.68 (C-4"), 136.23 (O-C=C-O), 138.86 (C-1"), 149.99 (C=N-); m.s., m/z (%): 517 (M^+, 0.8), 245 (3), 243 (3), 164 (43), 163 (43), 132 (100), 104 (25), 102 (20), 88 (34), 77 (57), 76 (62), 75 (52), 63 (35).

4,5-bis(4-bromophenyl)-2-phenylimino-1,3-dioxole (**5j**)

(92%), yellow prisms mp 147-148 °C. (Found: C, 53.73; H, 2.76; N, 3.00. $C_{21}H_{13}Br_2NO_2$ requires: C, 53.54; H, 2.78; N, 2.97); i.r. (Nujol): 1728, 1668, 1593, 1485, 1228, 1071, 1042, 1009, 939, 845, 828, 785, 750, 692 cm^{-1}; ^{1}H n.m.r. δ (CDCl$_3$, 200 MHz): 7.04 (m, 1H, H-4''), 7.17-7.27 (m, 4H, H-2'',3''), 7.29-7.42 (br m, 4H, H-2,2'), 7.47 (d, 4H, J = 8.4Hz, H-3,3'); ^{13}C n.m.r. δ (CDCl$_3$, 50.3 MHz): 123.25 (C-2''), 124.10 (C-4''), 124.31 (C-4,4'), 124.59 (br, C-1,1'), 127.95 (br, C-2,2'), 129.02 (C-3''), 132.39 (C-3,3'), 135.85, 136.09, (br, O-C=C-O), 143.65 (C-1''), 149.41 (C=N-); m.s., m/z (%): 469 (M$^+$, 1), 245 (6), 243 (7), 186 (13), 183 (12), 164 (63), 163 (67), 119 (89), 91 (100), 88 (42), 76 (59), 64 (54).

4,5-bis(4-bromophenyl)-2-(4-chlorophenylimino)-1,3-dioxole (**5k**)

(87%), white needles mp 205-207 °C. (Found: C, 49.73; H, 2.39; N, 2.78. $C_{21}H_{12}Br_2ClNO_2$ requires: C, 49.89; H, 2.39; N, 2.77); i.r. (Nujol): 1726, 1665, 1586, 1489, 1234, 1070, 1010, 833, 825, 760 cm^{-1}; ^{1}H n.m.r. δ (CDCl$_3$, 200 MHz): 7.19 (d, 2H, J = 8.6 Hz, H-2''), 7.29 (d, 2H, J = 8.6 Hz, H-3''), 7.35-7.48 (br m, 4H, H-2,2'), 7.55 (d, 4H, H-3,3'); ^{13}C n.m.r. δ (CDCl$_3$, 75.4 MHz, 40 °C): 124.54 (C-4,4'), 124.60 (C-2'', C-1,1'), 128.03 (C-2,2'), 129.12 (C-3''), 129.36 (C-4''), 132.53 (C-3,3'), 136.17 (O-C=C-O), 142.37 (C-1''), 149.69 (C=N-); m.s., m/z (%): 503 (M$^+$, 1), 245 (17), 243 (17), 185 (16), 183 (16), 164 (95), 163 (100), 155 (39), 153 (47), 125 (72), 90 (50), 88 (51), 76 (63), 75 (66), 63 (51).

2-(4-chlorophenylimino)-4,5-bis(2-methoxyphenyl)-1,3-dioxole (**5l**)

(93%), white needles mp 149-150 °C. (Found: C, 67.79; H, 4.42; N, 3.45. $C_{23}H_{18}ClNO_4$ requires: C, 67.73; H, 4.45; N, 3.43); i.r. (Nujol): 1730, 1672, 1501, 1487, 1283, 1252, 1222, 1060, 1024, 843, 762 cm^{-1}; ^{1}H n.m.r. δ (DMSO-d$_6$, 200 MHz, 75 °C): 3.42 (s, 6H, OCH$_3$), 6.96-7.05 (m, 4H, H-3,3',5,5'), 7.21 (d, 2H, J = 8.8 Hz, H-2''), 7.32 (d, 2H, J = 8.8 Hz, H-3''), 7.36-7.45 (m, 4H, H-4,4',6,6'); ^{13}C n.m.r. δ (DMSO-d$_6$, 50.3 MHz, 75 °C): 54.71 (OCH$_3$), 111.20 (C-3,3'), 115.15 (C-1,1'), 119.75 (C-5,5'), 124.11 (C-2''), 126.93 (C-4''), 128.25 (C-3''), 128.48 (C-6,6'), 130.82 (C-4,4'), 134.72 (O-C=C-O), 143.09 (C-1''), 150.34 (C=N-), 156.41 (C-2,2'); m.s., m/z (%): 409 (M$^+$ + 2, 7), 407 (M$^+$, 25), 244 (29), 239 (80), 211 (50), 209 (72), 165 (71), 155 (36), 153 (88), 152 (45), 135 (100), 125 (50), 91 (43), 77 (50).

4-methoxyphenyl-5-phenyl-2-phenylimino-1,3-dioxole (**7a**)

(87%, mixture of Z and E isomers) light brown viscous material (Found: C, 76.61; H, 4.96; N, 4.09. $C_{22}H_{17}NO_3$ requires: C, 76.95; H, 4.99; N, 4.08); i.r. (Nujol): 1729, 1678, 1597, 1516, 1494, 1302, 1256, 1177, 1066, 1027, 835, 762, 695 cm^{-1}; ^{1}H n.m.r. δ (CDCl$_3$, 200 MHz, 47 °C): 3.71 (s, 3H, OCH$_3$), 6.84 (d, 2H, J = 8.6 Hz, H-3'), 7.03 (m, 1H, H-4''), 7.21-7.33 (m, 7H, H-3,4,2'',3''), 7.41-7.57 (m, 4H, H-2,2'); ^{13}C n.m.r. δ (CDCl$_3$, 50.3 MHz, 47 °C): 55.14 (OCH$_3$), 114.41 (C-3'), 118.08 (C-1'), 123.16 (C-2''), 123.49 (C-4''), 126.05 (C-2), 128.22 (C-2'), 128.63, 128.68 (C-3,3''), 129.25 (C-4), 135.37 (4-CH$_3$O-C$_6$H$_4$-C=), 136.56 (C$_6$H$_5$-C=), 144.25 (C-1''), 149.95 (C=N-), 160.86 (C-4'); m.s., m/z (%): 343 (M$^+$, 45), 196 (66), 181 (74), 165

(37), 153 (52), 152 (63), 135 (55), 119 (32), 91 (44), 77 (100), 64 (35).

2-(4-chlorophenylimino)-4-methoxyphenyl-5-phenyl-1,3-dioxole (**7b**)

(84%, mixture of Z and E isomers), white mp 123-131 °C. (Found: C, 69.59; H, 4.26; N, 3.74. $C_{22}H_{16}ClNO_3$ requires: C, 69.94; H, 4.27; N, 3.71); i.r. (Nujol): 1745, 1669, 1607, 1513, 1490, 1259, 1227, 1178, 1067, 1024, 843, 758, 700, 612 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$, 200 MHz): 3.82 (s, 3H, OCH_3), 6.91 (d, 2H, J = 8.7 Hz, H-3'), 7.24 (d, 2H, J = 9.0 Hz, H-2''), 7.27 (d, 2H, J = 9.0 Hz, H-3''), 7.34-7.38 (m, 3H, H-3,4), 7.44-7.55 (m, 4H, H-2,2'); ^{13}C n.m.r. δ ($CDCl_3$, 50.3 MHz, 47 °C): 55.34 (OCH_3), 114.53 (C-3'), 118.05 (C-1')*, 124.61 (C-2''), 126.05 (C-1)*, 126.18 (C-2)*, 128.37 (C-2')*, 128.74 (C-4''), 128.83, 128.88 (C-3,3''), 129.52 (C-4), 135.60 (4-CH_3O-C_6H_4-C=)*, 136.77 (C_6H_5-C=)*, 142.92 (C-1''), 150.52 (C=N-), 160.98 (C-4') ; *The spectrum with the sample at ambient temperature (23 °C) shows splitting of each single signal; m.s., m/z (%): 379 (M^+ + 2, 34), 377 (M^+, 100), 196 (87), 181 (65), 165 (27), 153 (41), 152 (43).

2-(1,4-phenylenediimino)-bis(4,5-diphenyl-1,3-dioxole) (**8**)

(96%), white needles mp 169-171 °C. (Found: C, 78.53; H, 4.42; N, 5.08. $C_{36}H_{24}N_2O_4$ requires: C, 78.82; H, 4.41; N, 5.11); i.r. (Nujol): 1728, 1673, 1505, 1378, 1241, 1068, 1024, 937, 758, 691 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz, 40 °C): 7.32 (s, 4H, H-2''), 7.38-7.41 (m, 12H, H-3,3',4,4'), 7.60 (br s, 8H, H-2,2'); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz, 40 °C): 123.86 (C-2''), 126.12 (C-1,1'), 126.65 (br, C-2,2'), 128.90 (C-3,3'), 129.78 (C-4,4'), 136.37, 136.86 (O-C=C-O), 139.80 (C-1''), 149.83 (C=N-); m.s., m/z (%): 548 (M^+, 6), 415 (7), 354 (9), 166 (30), 165 (100), 105 (7), 77 (8).

Preparation of dioxolenones 6.

Products **5e**, **5j**, and **5l** (3 mmol), were stirred in TFA (5 mL) for 10 h at room temperature. The solutions were dropped onto ice. After neutralization with aqueous sodium hydroxide, solid products **7** were collected and crystallized from boiling aqueous acetonitrile.

4,5-bis(4-methoxyphenyl)-1,3-dioxol-2-one (**6a**)

(82%), white needles mp 174-176 °C. (Found: C, 68.41; H, 4.74. $C_{17}H_{14}O_5$ requires: C, 68.45; H, 4.73); i.r. (Nujol): 1807, 1605, 1525, 1509, 1454, 1307, 1258, 1237, 1183, 1069, 1024, 832, 759 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 3.84 (s, 6H, OCH_3), 6.92 (d, 4H, J = 9.0 Hz, H-3), 7.47 (d, 4H, J = 9.0 Hz, H-2); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 55.38 (OCH_3), 114.39 (C-3), 118.01 (C-1), 127.94 (C-2), 136.02 (O-C=C-O), 152.05 (C=O), 160.62 (C-4), m.s., m/z (%): 298 (M^+, 71), 226 (51), 211 (100), 183 (13), 168 (12), 152 (11), 135 (15).

4,5-bis(4-bromophenyl)-1,3-dioxol-2-one **(6b)**

(88%), pale yellow needles mp 147-149 °C. (Found: C, 45.46; H, 2.05. $C_{15}H_8Br_2O_3$ requires: C, 45.49; H, 2.04); i.r. (Nujol): 1812, 1665, 1587, 1398, 1223, 1068, 1008, 822, 762 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$, 200 MHz): 7.42 (d, 4H, J = 8.6 Hz, H-2), 7.56 (d, 4H, J = 8.6 Hz, H-3); ^{13}C n.m.r. δ ($CDCl_3$, 50.3 MHz): 124.22 (C-4), 124.69 (C-1), 127.95 (C-2), 132.51 (C-3), 136.54 (O-C=C-O), 151.15 (C=O); m.s., m/z (%): 366 (M^+ - 28, 1), 185 (100), 183 (89), 157 (24), 155 (23), 76 (11), 75 (10).

4,5-bis(2-methoxyphenyl)-1,3-dioxol-2-one **(6c)**

(79%), white needles mp 206-209 °C. (Found: C, 68.42; H, 4.73. $C_{17}H_{14}O_5$ requires: C, 68.45; H, 4.73); i.r. (Nujol): 1813, 1603, 1580, 1505, 1437, 1263, 1217, 1064, 1019, 757 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$, 200 MHz): 3.45 (s, 6H, OCH_3), 6.84 (d, 2H, J = 8.0 Hz, H-3), 6.96 (td, 2H, J_t = 8.0 Hz, J_d = 0.9 Hz, H-5), 7.33 (td, 2H, J_t = 8.0 Hz, J_d = 1.7 Hz, H-4), 7.41 (dd, 2H, J = 8.0 Hz, J = 1.7 Hz, H-6); ^{13}C n.m.r. δ ($CDCl_3$, 50.3 MHz): 54.93 (OCH_3), 110.47 (C-3), 116.56 (C-1), 120.26 (C-5), 129.00 (C-6), 131.00 (C-4), 136.03 (O-C=C-O), 152.72 (C=O) 156.74 (C-2); m.s., m/z (%): 298 (M^+, 100), 186 (16), 135 (37), 92 (16), 91 (15), 77 (28), 69 (16).

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20. IR and high field ^{1}H NMR spectra for crude and crystalline products were recorded and showed negligible differences.
21. The product corresponding to entry **5j** was isolated by extraction.
22. The product **8** was crystallized from chloroform-methanol.

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