Selective 1,4-Addition of Arenes to 3-Chloro-3-cyclobutene-1,2-dione under Friedel−Crafts Conditions. Synthesis and Reactivity of 4-Aryl-3-chloro-2-hydroxy-2-cyclobuten-1-ones[1]

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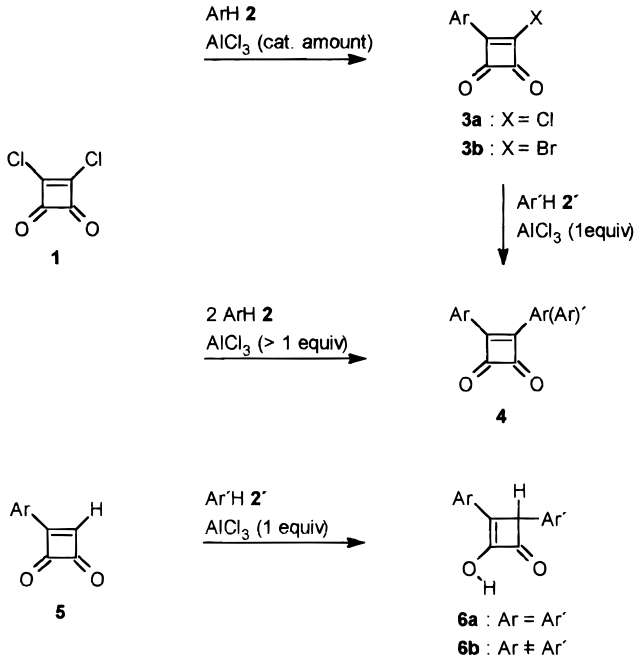
The reaction of semisquaric chloride **(7)** with arenes **2** has been investigated. In the presence of 1.1 equiv of $AlCl_3$ and in the temperature range of −15° C to rt the arenes **2a-q** afford the 4-aryl-3-chloro-2-hydroxy-2-cyclobuten-1-ones (chloroenols) **8a-q** in good yield. By contrast, **7** reacts with 1,4-dimethoxybenzene **(2l)** in boiling CH_2Cl_2 to give a mixture of (2,5-dimethoxyphenyl)cyclobutenedione **(9a)** (27% yield) and bis(2,5-dimethoxyphenyl)cyclobutenedione **(10a)** (8% yield). With 1,2,4-trimethoxybenzene **(2r)** in the presence of trifluoroacetic acid is generated (2,4,5-trimethoxyphenyl)-cyclobutenedione **(9b)** in 21% yield. The chloroenols **8** allow a series of valuable transformation reactions: with diazomethane the chloroenol methyl ethers **11** are generated, with chlorine the 3-aryl-4-chlorocyclobutenediones **12**, and with bromine in MeOH the 3-aryl-4-methoxycyclobutenediones **13**. In DMSO or in acetone/H_2O the chloroenols **8** eliminate HCl, furnishing the arylcyclobutenediones **14**. In a mixture of acetone-d_6/D_2O/DCl are obtained 4-aryl-cyclobutenediones-3-*d* **15**. For the latter two processes the corresponding 3-aryl-4-chlorocyclobutane-1,2-diones **16** are postulated as intermediates. Thermolysis of the chloroenols **8** and the chloroenol methyl ethers **11** in refluxing *m*-xylene afforded the 3-chloro-1,2-dihydroxynaphthalenes **17** and the 3-chloro-1-hydroxy-2-methoxynaphthalenes **18**, respectively.

Introduction

A great number of investigations have been made into the reaction of substituted cyclobutenediones with arenes **2** under Friedel−Crafts conditions. In such reactions halogenocyclobutenediones react as vinylogous acid halogenides. Thus, 3,4-dichlorocyclobutenedione (squaric dichloride) **(1)** affords 3-aryl-4-chlorocyclobutenediones **3a** or diarylcyclobutenediones **4**, depending upon the amount of catalyst ($AlCl_3$), the molar ratio of the educts, and the reaction conditions (Scheme 1).[2−4] Accordingly, the 3-aryl-4-halogenocyclobutenediones **3a** and **3b** react with arenes **2′** to give the diarylcyclobutenediones **4**.[2g,5] Monosubstituted cyclobutenediones such as **5**, on the other hand, behave as vinylogous aldehydes. They react with arenes in the presence of 1 equiv of $AlCl_3$ to give 2-hydroxy-2-cyclobuten-1-ones **6a** and **6b**.[2g,5,6]

In this context it was of interest to examine in which way 3-chloro-3-cyclobutene-1,2-dione (semisquaric chloride) **(7)**,[7] which combines the structural elements of a vinylogous carboxylic acid chloride and a vinylogous aldehyde, would react with arenes **2** under Friedel−Crafts conditions.

Scheme 1



Results and Discussion

Synthesis of 4-Aryl-2-hydroxycyclobutenones (Chloroenols). Semisquaric chloride **(7)** was reacted with equimolar amounts of benzene **(2a)** and $AlCl_3$ in 1,2-dichloroethane. While a complex mixture of products was generated when heating the reaction mixture, at −15 °C (30 min, and then rt, 4.5 h) we obtained 3-chloro-2-hydroxy-4-phenyl-2-cyclobuten-1-one **(8a)** in almost quantitative yield (96%). The structure of **8a** was confirmed by spectroscopic methods. The mass spectrum of **8a** exhibited molecular ions at $m/z = 196$ (15%) and $m/z = 194$ (45%). The IR spectrum exhibited a broad absorption at 3300−3100 cm^{-1} due to a chelated OH group and a strong C=O absorption at 1750 cm^{-1}. The ^1H NMR spectrum was characterized by a signal at δ 4.47, corresponding to the proton in the 4-position of the cyclobutenone system. Finally, the ^{13}C NMR spectrum

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(1) Oxocarbons and Related Compounds; Part 23. Part 22: Schmidt, A. H.; Kircher, G.; Künz, Ch.; Wahl, S.; Hendriok, M. W. *J. Org. Chem.* **1995**, *60*, 3890.

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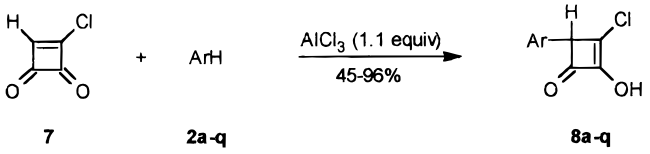
Scheme 2



7 **2a-q** **8a-q**

Table 1. 4-Aryl-3-chloro-2-hydroxy-2-cyclobuten-1-ones 8 Obtained by the Addition of Arenes to Semisquaric Chloride (7)

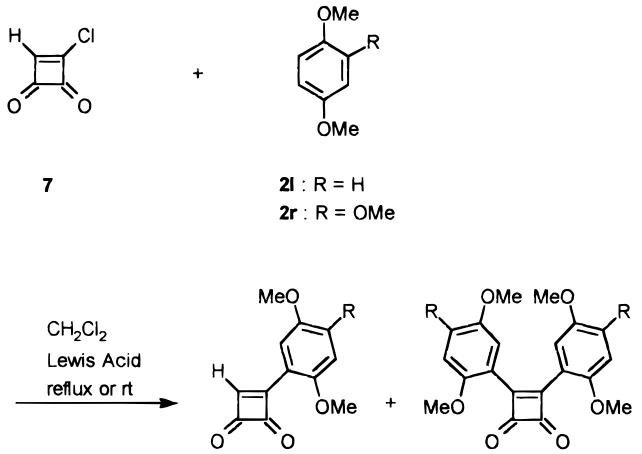
entry	Ar	temp (°C)/time (h)	product	yield[a] (%)
1	phenyl	−15/0.5, then rt/4.5	**8a**	96
2	*p*-tolyl	−15/0.5, then rt/4.5	**8b**[b]	79
3	4-isopropylphenyl	−15/0.5, then rt/4.5	**8c**	77
4	4-*tert*-butylphenyl	−15/0.5, then rt/6	**8d**	70
5	4-methoxyphenyl	−15/2	**8e**	47
6	4-chlorophenyl	−15/0.5, then rt/6	**8f**	90
7	4-bromophenyl	−15/0.5, then rt/6	**8g**	47
8	4-iodophenyl	−15/0.5, then rt/6	**8h**	80
9	2,4-dimethylphenyl	−15/0.5, then rt/4.5	**8i**	67
10	2,5-dimethylphenyl	−15/0.5, then rt/4.5	**8j**	95
11	3,4-dimethoxyphenyl	−15/5	**8k**	89
12	2,5-dimethoxyphenyl	−15/5	**[8l]**[c]	−
13	2,5-dichlorophenyl	−15/0.5, then rt/48	**8m**	90
14	2,3,4-trimethylphenyl	−15/2.5	**8n**	45
15	mesityl	−15/3	**8o**	69
16	2,3,4,5-tetramethyl-phenyl	−15/2.5	**8p**	93
17	naphthalen-1-yl	−15/0.5, then rt/4.5	**8q**[d]	85

[a] Yields represent crude yields of products (ca. 90−95% pure by ^{1}H NMR) except for products **8a**, **8c, 8e, 8f, 8g**, and **8m**, which are isolated, recrystallized yields. [b] **8b** was accompanied by ca. 15% 3-chloro-2-hydroxy-4-(*o*-tolyl)-2-cyclobuten-1-one. The ratio of products was not substantially changed by repeated recrystallizations. [c] Isolated at −15 °C; not characterized due to thermal instability. [d] On the basis of ^{1}H NMR measurements we ascribe, tentatively, the attack of **7** on naphthalene at the 1-position. Chemical proof of this orientation is being pursued.

exhibited 8 signals (4 C_q and 4 C_{tert}), which is in agreement with the structure of **8a**. As illustrated in Scheme 2 and summarized in Table 1, the reaction of semisquaric chloride **(7)** with benzene **(2a)** can be extended to a large number of arenes containing one or several substituents.

As can be seen from Table 1 it is necessary to adapt the reaction conditions to the electron density of the individual arene to obtain good product yields. Thus, the reactions with the halobenzenes **2f-h** and **2m** (entries 6−8 and 13) were carried out mainly at rt, while the reactions with the methoxybenzenes **2e**, **2k**, and **2l** (entries 5, 11, and 12) were conducted at −15°C. No reaction took place with electron poor aromatics (acetophenone, nitrobenzene, (trichloromethyl)benzene, (trifluoromethyl)benzene). With the exception of 3-chloro-4-(4-methoxyphenyl)-2-hydroxy-3-cyclobuten-1-one **(8e)**, 4-(4-bromophenyl)-3-chloro-2-hydroxy-3-cyclobuten-1-one **(8g)**, and 3-chloro-4-(2,3,4-trimethylphenyl)-2-hydroxy-3-cyclobuten-1-one **(8n)**, the chloroenols **8** were obtained in good to excellent yields. The chloroenols **8a-q**[8] are white to off-white solids, which decompose easily at rt, with the exception of **8m**. The chloroenol **8l** obtained from the reaction of **7** with 1,4-dimethoxybenzene **(2l)** could be isolated at −15 °C; brought to rt it decomposed rapidly with vigorous elimination of HCl. On the other hand, 3-chloro-(2,5-dichlorophenyl)-2-hydroxy-2-cyclobuten-1-one **(8m)** was stable and could be stored at rt. The thermal instability of the other chloroenols **8** was intermediate between these two. In agreement with these findings several chloroenols **(8b**, **8f**, **8g**, **8o**, **8p)** did not analyze correctly. These investigations gave no indication of the generation of 3-aryl-3-cyclobutene-1,2-diones as byproducts of the chloroenols **8**. However, in further experiments[2n] it was found that semisquaric chloride **(7)** reacts with 1,4-dimethoxybenzene **(2l)** in the presence of $AlCl_3$ with heating to give a mixture of the monoarylated and the diarylated cyclobutenedione **9a** and **10a**, respectively. On reaction of semisquaric chloride **(7)** with 1,2,4-trimethoxybenzene **(2r)** in the presence of trifluoroacetic acid (rt, 24 h) we furthermore obtained 3-(2,4,5-trimethoxyphenyl)-3-cyclobutene-1,2-dione **(9b)** in 21% yield (Scheme 3).[9]

Scheme 3



7 **2l** : R = H; **2r** : R = OMe

9a : R = H (27%) **10a** : R = H (8%)
9b : R = OMe (21%)

Reactivity of the 4-Aryl-2-hydroxycyclobutenones (Chloroenols). Since satisfactory elemental analyses were not obtained for several chloroenols **8**, and to explore their reactivity, several representatives were treated with diazomethane. This yielded the chloroenol methyl ethers **11** (Scheme 4), which were characterized by correct elemental analyses. Their structure was confirmed by spectroscopic methods (see Experimental Section).

Further investigations into the reactivity of the chloroenols **8** proved them valuable four-membered-ring

(2) For publications dealing completely or in part with the reaction of squaric dichloride with aromatics and offering full to almost no experimental details, see: (a) Maahs, G.; Hegenberg, P. *Angew. Chem.* **1966**, *78*, 927; *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 888. (b) DeSelms, R. C.; Fox, C. J.; Riordan, R. C. *Tetrahedron Lett.* **1970**, 781. (c) Becher, H. J.; Fenske, D.; Langer, E. *Chem Ber.* **1973**, *106*, 177. (d) Green, B. R.; Neuse, E. W. *Synthesis* **1974**, 46. (e) Neuse, E. W.; Green, B. *J. Org. Chem.* **1974**, *39*, 1585. (f) Wendling, L. A.; Koster, S. A.; Murray, J. E.; West, R. *J. Org. Chem.* **1977**, *42*, 1126. (g) Ried, W.; Vogl, M. *Liebigs Ann. Chem.* **1977**, 101. (h) Argyropoulos, N. G. *Chem. Chron.* (*New Series*) **1986**, *15*, 119. (i) Kazmaier, P. M.; Burt, R. A.; Baranyi, G. US Patent 4, 624, 904, 25. Nov. 1986; Xerox Corp., USA; *Chem. Abstr.* **1987**, *106*, 205165m. Described here, with full experimental details, is the preparation of 3-chloro-4-[4-(*N,N*-dimethylamino)phenyl]-cyclobutenedione by the reaction of squaric dichloride **(1)** (1 equiv) with *N,N*-dimethylaniline (0.33 equiv) in the presence of $AlCl_3$ (3 equiv). Yield 33%; mp 190−191 °C. (j) Akasaki, Y.; Tokida, A.; Torigoe, K.; Imai, A. Japanese Patent 62,249,952; 30 Oct 1987; Fuji Xerox Co., Ltd., Japan; *Chem. Abstr.* **1988**, *109*, 170005s. Described here is the preparation and characterization of fourteen 3-[4-(*N,N*-dialkylamino)-phenyl]-4-chlorocyclobutenediones. The reaction between squaric dichloride **(1)** and the *N,N*-dialkylaniline is carried out in the presence of BF_3-etherate. However, the reaction proceeded more satisfactorily without a catalyst. Thus, the desired compound is obtained in higher purity than the product obtained in the presence of a Lewis acid catalyst. (k) Akasaki, Y.; Tokida, A.; Saeki, S.; Torigoe, K.; Imai, A. Japanese Patent 62,249,953; 30 Oct 1987; Fuji Xerox Co., Ltd., Japan; *Chem. Abstr.* **1988**, *109*, 170004r. (l) Akasaki, Y.; Tokida, A.; Torigoe, K.; Imai, A. Japanese Patent 01,146,865; 8 June 1989; Fuji Xerox Co., Ltd., Japan; *Chem. Abstr.* **1989**, *111*, 232571a. (m) Matsuoka, M; Soejima, H.; Kitao, T. *Dyes and Pigments* **1991**, *16*, 309. (n) Maus, St. *Diplomarbeit*; Fachhochschule Fresenius: Wiesbaden, 1994.

Scheme 4

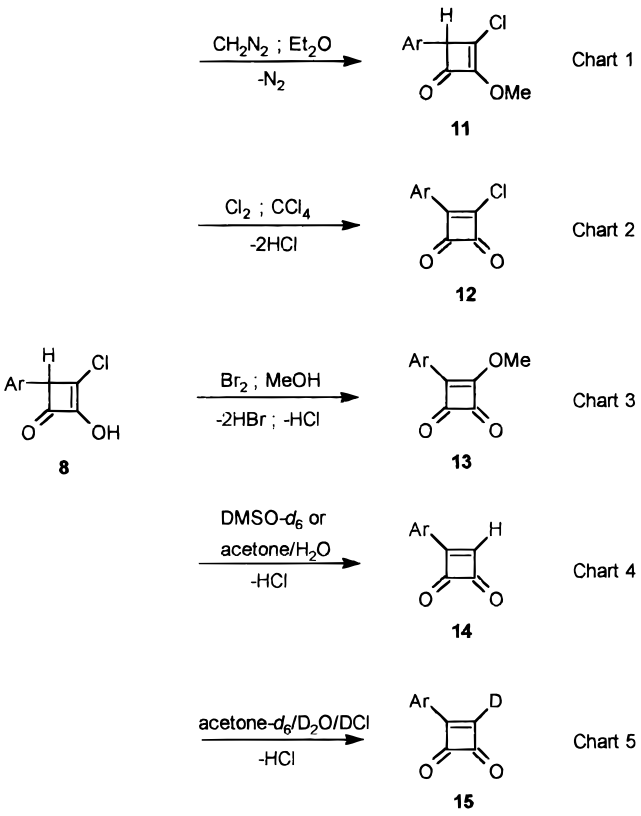


Chart 1.
4-Aryl-3-chloro-2-methoxy-2-cyclobuten-1-ones 11

11	Ar	11	Ar
11a	C_6H_5	**11f**	4-IC_6H_4
11b	4-MeC_6H_4	**11g**	2,5-$(MeO)_2C_6H_3$
11c	4-*t*-BuC_6H_4	**11h**	2,5-$Cl_2C_6H_3$
11d	4-$MeOC_6H_4$	**11i**	2,3,4,5-Me_4C_6H
11e	4-ClC_6H_4	**11j**	naphthalen-1-yl

Chart 2.
3-Aryl-4-chloro-3-cyclobutene-1,2-diones 12

12	Ar	12	Ar
12a	C_6H_5	**12e**	4-ClC_6H_4
12b	4-MeC_6H_4	**12f**	2,5-$Me_2C_6H_3$
12c	4-*t*-BuC_6H_4	**12g**	2-Cl-4,5-$(MeO)_2C_6H_2$[a]
12d	4-$MeOC_6H_4$		

[a] Obtained from the chlorination of **8k**.

synthons. As illustrated in Scheme 4, the chloroenols **8** can be dehydrogenated by chlorine to give the 3-aryl-4-chlorocyclobutenediones **12** (Chart 2). The treatment of 4-(3,4-dimethoxyphenyl)-2-hydroxy-2-cyclobuten-1-one **(8k)** with chlorine deserves special mention. In this case not only dehydrogenation, but also chlorination of the aryl substituent was observed. The ^{1}H NMR spectrum provided clear evidence that 3-chloro-4-(2-chloro-4,5-dimethoxyphenyl)-3-cyclobutene-1,2-dione **(12g)** had been generated. In the ^{1}H NMR spectrum the two protons of the aryl ring appear as two singlets at δ 7.01 and 7.38. A coupling of these protons is not observed, thus excluding another arrangement of the substituents in the phenyl ring.

Chart 3.
3-Aryl-4-methoxy-3-cyclobutene-1,2-diones 13

13	Ar	13	Ar
13a	C_6H_5	**13c**	4-ClC_6H_4
13b	4-MeC_6H_4		

Chart 4.
3-Aryl-3-cyclobutene-1,2-diones 14

14	Ar	14	Ar
14a	C_6H_5[a,b]	**14h**	2,4-$Me_2C_6H_3$[a]
14b	4-MeC_6H_4[a,c]	**14i**	2,5-$Me_2C_6H_3$[a,c]
14c	4-*i*-PrC_6H_4[a]	**14j [=9a]**	2,5-$(MeO)_2C_6H_3$[c]
14d	4-*t*-BuC_6H_4[a,c]	**14k**	2,5-$Cl_2C_6H_3$[a,c]
14e	4-$MeOC_6H_4$[a,c]	**14l**	2,3,4-$Me_3C_6H_2$[a]
14f	4-ClC_6H_4[a,c]	**14m**	2,3,4,5-Me_4C_6H[a]
14g	4-BrC_6H_4[a,c]	**14n**	naphthalen-1-yl[a,c]

[a] Method A: **14** was obtained quantitatively in solution (DMSO-d_6, rt, 24 h) from the corresponding **8**. Proof of structure was accomplished by ^{1}H and ^{13}C NMR spectroscopy. No physical data taken. [b] Method B: Reaction carried out in DMSO. Product isolated. Physical and spectroscopic data obtained. [c] Method C: Reaction carried out in acetone/water. Product isolated. Elemental analysis, physical and spectroscopic data obtained.

Chart 5.
4-Aryl-3-cyclobutene-1,2-diones-3-*d* 15[a]

15	Ar	15	Ar
15a	C_6H_5	**15c**	4-*t*-BuC_6H_4
15b	4-MeC_6H_4	**15d**	4-ClC_6H_4

[a] Incorporation of 1 D/mol indicated by ^{1}H NMR: **15a**: 87%; **15b**: 75%; **15c**: 75%; **15d**: 95%.

Besides the intensively investigated parent compound, 3-chloro-4-phenylcyclobutenedione **(12a)**,[10] and several representatives with simple substituent-patterns in the phenyl ring,[4g,11,12] a large number of 3-[4-(*N,N* dialkyamino)phenyl]-4-chlorocyclobutenediones[4] have been prepared. They are easily transformed into the corresponding 3-aryl-4-hydroxycyclobutenediones, which are of great interest as starting materials for the synthesis of squaraines.[13]

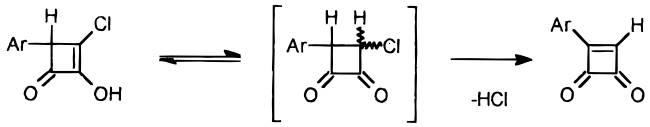
When the dehydrogenation of the chloroenols **8** was carried out with bromine and using methanol as the

(3) The results reported in the literature on the reaction of squaric dichloride **(1)** with benzene **(2a)** are partly contradictory: See refs 2a and 2c. Furthermore, we were not able to establish one of the published procedures as a general one for the generation of 3-aryl-4-chlorocyclobutenediones **12**: Schmidt, A. H.; unpublished results. See also ref 2n.

solvent, 3-aryl-4-bromo-cyclobutenediones were generated as intermediates. Because of their high reactivity they experienced methanolysis, and the 3-aryl-4-methoxycyclobutenediones **13a**,[10] **13b**, and **13c** were isolated (Chart 3).

On measuring ^{1}H NMR spectra of the chloroenols **8**, we observed that solutions of **8** in DMSO-d_6 were unstable. Within 24 h at rt the chloroenols **8** eliminated HCl and were transformed into the corresponding 3-aryl-cyclobutene-1,2-diones **14**[12] (method A) (Chart 4). This finding led to a novel, preparatively simple means of access to this class of compounds: the chloroenol **8a** was dissolved in DMSO and the solution kept at rt for 24 h and then poured onto ice. Phenylcyclobutenedione **14a**[10] precipitated and was isolated in 41% yield (method B). In an optimized variant, the solution of a chloroenol **8** in acetone/water was heated to reflux for 1.5 h. On cooling, the arylcyclobutenedione **14** crystallized from the reaction mixture (method C). We assume that the chloroenols **8** exist in a tautomeric equilibrium with the corresponding

Scheme 5



8 **16** **14**

3-aryl-4-chlorocyclobutane-1,2-diones **16** in the above mentioned solvents. In an irreversible reaction HCl is eliminated from the latter compounds, whereby the 3-aryl-cyclobutenediones **14** are formed[14] (Scheme 5).

In agreement with this, heating of the chloroenols **8** in a mixture of acetone-d_6/D_2O/DCl or acetone-d_6/D_2O afforded 4-aryl-cyclobutene-1,2-diones-3-*d* **15** (Scheme 4, Chart 5). Incorporation of approximately 1 D/mol in the products **15a-d** was indicated by ^{1}H NMR analyses.

Thermal Isomerization of 4-Aryl-2-hydroxy [and 2-methoxy]-cyclobutenones. Liebeskind[15] *et al.* and Moore[16] *et al.* have investigated the thermally induced isomerization of 4-aryl [and 4-hetaryl]-4-hydroxycyclobutenones and subsequently of 4-aryl-4-substituted-cyclobutenones[17] in depth and have developed this process into a valuable method for the preparation of 1,4-dihydroxynaphthalenes, 1,4-naphthoquinones, and α-naphthols.[18,19] Their work prompted us to investigate, whether the 4-aryl-2-hydroxycyclobutenones (chloroenols) **8** were also susceptible to this rearrangement. On heating solutions of the chloroenols **8** in *m*-xylene to reflux for 3 h we obtained the 3-chloro-1,2-dihydroxynaphthalenes **17a**,[20] **17b**, and **17d-g** in moderate to good yields. **8c** constituted an exception, and, under the same conditions, afforded a brown oil, consisting of several compounds which were difficult to separate. The generation of hitherto unknown 3-chloro-1,2-dihydroxyphenanthrene **(17h)** according to this method deserves special mention. The reactions are illustrated in Scheme 6 and the results are summarized in Table 2. The thermal

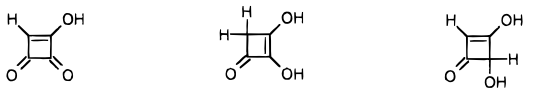
(4) In extension of the patent cited in ref 2j, several recent patents and papers describe the preparation of a large number of new 3-[4-(*N*,*N*-dialkylamino)phenyl]-4-chloro-3-cyclobutene-1,2-diones as well as structurally related compounds. For selected references, see: (a) Nakazumi, H. Japanese Patent 06,184,109; 5 July 1994; Mitsubishi Chem. Ind., Japan. *Chem. Abstr.* **1995**, *122*, 132976v. (b) Nakazumi, H. Japanese Patent 06,184,134; 5 July 1994; Mitsubishi Chem. Ind., Japan. *Chem. Abstr.* **1995**, *122*, 105672m. (c) Nishikata, Y.; Tomono, T.; Fu, R. Japanese Patent 06,100,511; 12. April 1994; Fuji Xerox Co., Ltd., Japan; *Chem. Abstr.* **1994**, *121*, 121397k. (d) Chen, H.; Herkstroeter, W. G.; Perlstein, J.; Law, K.-Y.; Whitten, D. G. *J. Phys. Chem.* **1994**, *98*, 5138. (e) Kitipichai, P.; La Peruta, R.; Korenowski, G. M.; Wnek, G. E. *J. Polymer. Sci., Part A: Polym. Chem.* **1993**, *31*, 1365. (f) Fu, R. Japanese Patent 04,202,166; 22. July 1992; Fuji Xerox Co., Ltd., Japan; *Chem. Abstr.* **1992**, *117*, 261281k. (g) Fu, R. Japanese Patent 04,202,165; 22 July 1992; Fuji Xerox Co., Ltd., Japan; *Chem. Abstr.* **1992**, *117*, 261280j. (h) Akasaki, Y.; Tokida, A.; Torigoe, K.; Imai, A. Japanese Patent 01,146,848; 8 June. 1989; Fuji Xerox Co., Ltd., Japan; *Chem. Abstr.* **1989**, *111*, 232276h. (i) Akasaki, Y.; Torigoe, K.; Imai, A.; Tokida, A.; Saeki, S. Japanese Patent 62,249,951; 30 Oct 1987; Fuji Xerox Co., Ltd., Japan; *Chem. Abstr.* **1988**, *109*, 210668u.

(5) Ried, W.; Schäfer, D. P. *Chem. Ber.* **1969**, *102*, 4193. Presented here are also mechanistic details on the reactions of 3-chloro-4-phenylcyclobutene-1,2-dione and 3-phenylcyclobutene-1,2-dione with arenes under Friedel−Crafts conditions.

(6) (a) Ried, W.; Schmidt, A. H.; Kuhn, W. *Chem Ber.* **1971**, *104*, 2622. (b) Ried, W.; Knorr, H.; Kuhn, W.; Weissert, U. *Chem Ber.* **1975**, *108*, 1413.

(7) Schmidt, A. H.; Debo, M.; Wehner, B. *Synthesis* **1990**, 237.

(8) The chloroenols **8** may be characterized by their "oxidation number" (Bellus, D.; Fischer, H.; Greuter, H.; Martin, P. *Helv. Chim. Acta* **1978**, *61*, 1784.) (ON 5) and may be regarded as derivatives of the hitherto unknown 1,4-dihydrosemisquaric acid **II** (ON 5). It must be pointed out that 1,4-dihydrosemisquaric acid **II** and semisquaric acid **I** (ON 6) posess the same oxidation numbers as hydroquinone (ON 5) and *p*-benzoquinone (ON 6). One further vinylogous acid having the ON 5, derives from semisquaric acid: the 1,2-dihydrosemisquaric acid **III**. Like **II**, acid **III** is also hitherto unknown. However, derivatives E. g.: Heerding, J. M.; Moore, H. W. *J. Org. Chem.* **1991**, *56*, 4048 of **III** have already been described.



I **II** **III**

(9) We are actively involved at the present time in finding out (a) conditions, (b) catalysts, and/or (c) substituent patterns of arenes **2** which allow the production of 3-arylcyclobutenediones **14** on a preparative scale by reacting **7** with **2**.

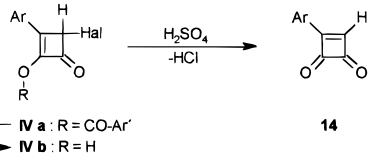
(10) Smutny, E. J.; Caserio, M. C.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 1793.

(11) Bellus, D. *J. Am. Chem. Soc.* **1978**, *100*, 8026.

(12) For reviews on phenyl- and arylcyclobutenediones and their derivatives, see: (a) Ried, W.; Schmidt, A. H. *Angew. Chem.* **1972**, *84*, 1048. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 997. (b) Schmidt, A. H.; Ried, W. *Synthesis* **1978**, 1. (c) Knorr, H.; Ried, W. *Synthesis* **1978**, 649.

(13) For reviews on squaraines, see : (a) Sprenger, H. E.; Ziegenbein, W. *Angew. Chem.* **1968**, *80*, 541. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 530. (b) Schmidt, A. H. *Synthesis* **1980**, 961. (c) Schmidt, A. H. In *Oxocarbons*, West, R., Ed.; Academic Press: New York, 1980; Chapter 10, p 185. (d) Law, K-Y. *Chem. Rev.* **1993**, *93*, 449.

(14) The conversion of 2-(aroyloxy)-4-halogeno-3-aryl-2-cyclobuten-1-ones **IVa** into arylcyclobutenediones **14** by treatment with sulfuric acid (ref a) obviously occurs *via* **IVb** and offers early examples of the "*3-halogeno [and 4-halogeno]-2-hydroxy-2-cyclobuten-1-one → cyclobutenedione conversion*", including a halogenocyclobutane-1,2-dione as an intermediate. (a) Schmidt, A. H. Dissertation, Universität Frankfurt am Main, 1970. (b) Ref 6a. (c) Schmidt, A. H.; Ried, W.; Gildemeister, H. *Liebigs Ann. Chem.* **1976**, 705.



IV a : R = CO-Ar′
IV b : R = H

14

(15) For selected references, see: (a) Liebeskind, L. S.; Iyer, S.; Jewell, C. F., Jr. *J. Org. Chem.* **1986**, *51*, 3065. (b) Liebeskind, L. S. *Tetrahedron* **1989**, *45*, 3053. (c) Liebeskind, L. S.; Zhang, J. *J. Org. Chem.* **1991**, *56*, 6379. (d) Liebeskind, L. S.; Granberg, K. L.; Zhang, J. *J. Org. Chem.* **1991**, *57*, 4345. (e) Gurski Birchler, A.; Lin, F.; Liebeskind, L. S. *J. Org. Chem.* **1994**, *59*, 7737.

(16) For selected references, see: (a) Perri, S. T.; Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Org. Chem.* **1986**, *51*, 3067. (b) Moore, H. W.; Perri, S. T. *J. Org. Chem.* **1988**, *53*, 996. (c) Perri, S. T.; Rice, P.; Moore, H. W. *Org. Synth.* **1990**, *69*, 220. (d) Enhsen, A.; Karabelas, K. Heerding, J. M.; Moore, H. W. *J. Org. Chem.* **1990**, *55*, 1177. (e) Heerding, J. M.; Moore, H. W. *J. Org. Chem.* **1991**, *56*, 4048. (f) Gayo, L. M.; Winters, M. P.; Moore, H. W. *J. Org. Chem.* **1992**, *57*, 6896.

(17) (a) Xu, S. L.; Moore, H. W. *J. Org. Chem.* **1989**, *54*, 4024. (b) Xu, S. L. Moore, H. W. *J. Org. Chem.* **1992**, *57*, 326.

(18) For an application of this methodology, see: Selwood, D. L.; Jandu, K. S. *Heterocycles* **1988**, *27*, 1191.

(19) For a review on the construction of complex organic molecules by thermally induced ring expansion of 4-hydroxy-2-cyclobuten-1-ones, see: Moore, H. W.; Yerxa, B. R. *Chemtracts: Org. Chem.* **1992**, *5*, 273.

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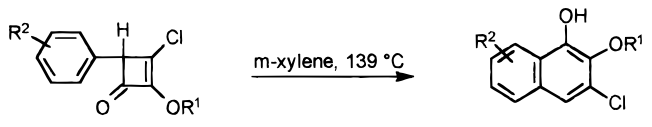
Scheme 6



8 : R^1 = H
11 : R^1 = Me

17 : R^1 = H
18 : R^1 = Me

isomerization described previously could be extended to 4-aryl-2-methoxycyclobutenones **11**. To our great satisfaction, the isomerization of the 3-chloro-2-methoxycyclobutenones **11** proceeded even more smoothly than that of the corresponding 3-chloro-2-hydroxycyclobutenones **8**.

We realized furthermore that the 3-chloro-1-hydroxy-2-methoxynaphthalenes **18a-f** were generated in high purity and with good yields (Scheme 6; Table 2). The 3-chloro-1-hydroxynaphthalenes **18**, selectively methoxylated in the 2-position represent a class of naphthalene derivatives with a novel substitution pattern. Related work has recently been published by Gurski and Liebeskind.[21] They have prepared 4-aryl-3-organyl-2-cyclobuten-1-ones by the 1,4-addition of organocopper reagents to monosubstituted cyclobutenediones and rearranged them at 140 °C for 20 h to give 3-organyl-2-(1,3,6-trioxaheptyl)-1-naphthols.

Conclusions

In summary, we have presented the synthesis of easily accessible 4-aryl-3-chloro-2-hydroxy-2-cyclobuten-1-ones **8**. They are distinguished by a unique substitution pattern and have proved to be versatile synthons for the preparation of arylcyclobutenediones and their derivatives. Furthermore, we have added a "Friedel−Crafts approach", starting with semisquaric chloride **(7)** and leading to 4-aryl-2-hydroxycyclobutenones, to the widely used "aryllithium approach" for the preparation of 4-aryl-4-hydroxycyclobutenones. The thermal isomerization of the 4-aryl-2-hydroxycyclobutenones and that of their methyl ethers affords 1,2-dihydroxy [and 1-hydroxy-2-methoxy]-naphthalenes, respectively, thus enlarging substantially the repertoire of naphthalene derivatives obtainable by the thermal isomerization of 4-arylcyclobutenones. The syntheses and the thermal isomerizations of 4-substituted-2-hydroxycyclobutenones with more complex and polynuclear aromatic substituents, as well as representatives with heterocyclic and nonaromatic substituents, are currently under investigation.

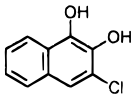
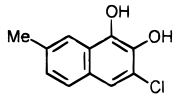
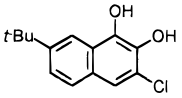
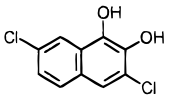
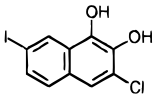
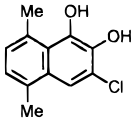
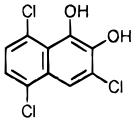
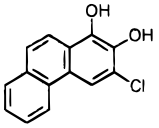
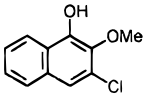
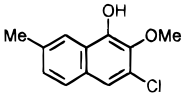
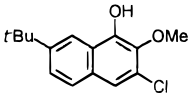
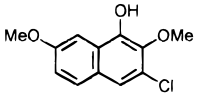
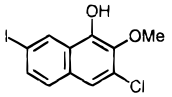
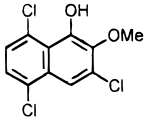
Experimental Section

Melting points were measured in capillary tubes and are uncorrected. IR spectra were recorded as solids in KBr pellets. Mass spectra were determined by electron impact at an ionizing voltage of 70 eV. ^{1}H NMR spectra were recorded at 400 MHz using TMS and/or $CDCl_3$ as internal standard. ^{13}C NMR spectra were recorded at 100.6 MHz using $CDCl_3$ or DMSO-d_6 as solvent and as internal standard (δ = 76.99 and δ = 39.50, respectively), unless otherwise stated. Elemental analyses were performed by the Institute of Chemistry, University of Mainz. Analytical thin layer chromatography was performed on precoated sheets of silica gel (silica gel 60, F 254, layer thickness 0.2 mm; Riedel de Haen, Seelze). Column chromatography was performed with silica gel (silica gel 60, 70−230 mesh; Merck, Darmstadt). The abbreviation "rt" is used for ambient temperature.

Starting Materials. Semisquaric chloride **(7)** was obtained by reacting semisquaric acid[22] with phosgene[7] or with oxalic

(21) Gurski, A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 6101.
(22) (a) Schmidt, A. H.; Maibaum, H. *Synthesis* **1987**, 134. Improved procedure: (b) Schmidt, A. H.; Künz, Ch.; Debo, M.; Mora-Ferrer, J. P. *Synthesis* **1990**, 819.

Table 2. Data for 3-Chloro-1,2-dihydroxynaphthalenes 17 and 3-Chloro-1-hydroxy-2-methoxynaphthalenes 18 Obtained by Thermal Isomerization of 4-Aryl-3-chloro-2-hydroxy [and 2-methoxy]-cyclobuten-1-ones 8 and 11

educt	product		yield (%)	mp. (°C)
8a	**17a**		82	111-112
8b	**17b**		80	160-162
8d	**17c**		--	--
8f	**17d**		71	172-173
8h	**17e**		66	148
8j	**17f**		56	95-96
8m	**17g**		79	166-167
8q	**17h**		64	168-170
11a	**18a**		64	80-81
11b	**18b**		81	84-86
11c	**18c**		75	84-85
11d	**18d**		75	106-107
11f	**18e**		81	123-125
11h	**18f**		71	139-140

dichloride.[23] All aromatics **2** were commercially available and were used as received.

3-Chloro-2-hydroxy-4-phenyl-2-cyclobuten-1-one (8a) (Table 1, Entry 1). Typical Procedure. A solution of semisquaric chloride **(7)** (2.32 g, 20 mmol) and benzene **(2a)** (1.57 g, 20 mmol) in 1.2-dichloroethane (30 mL) was cooled to −15 °C with magnetic stirring. $AlCl_3$ (2.92 g, 22 mmol) was added portionwise over 5 min, and the reaction mixture was stirred at this temperature for 30 min. The temperature was then raised to rt, and stirring was continued for further 4.5 h. During this period the reaction mixture took on a dark brown color. It was poured onto a mixture of crushed ice (150 g) and concd HCl (10 mL). The mixture was diluted with ether (100 mL). The organic layer was separated, and the aqueous layer was extracted with ether (3 × 60 mL). The combined organic layers were dried over $MgSO_4$. On evaporation *in vacuo* a solid remained and was recrystallized to give **8a**: white crystals; mp 147 °C dec (toluene); yield 3.74 g (96%); IR 3080−3020 (s, br), 1760 (vs), 1620 (s) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.47 (s, 1H), 7.22−7.44 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 62.04, 127.26, 128.30, 128.88, 134.09, 136.76, 148.43, 185.93; MS *m/z* (relative intensity) 196 (M^+, 15), 194 (M^+, 45), 159 (34), 131 (100), 102 (85). Anal. Calcd for $C_{10}H_7ClO_2$: C, 61.27; H, 3.63; Cl, 18.26. Found: C, 61.68; H, 3.54; Cl, 18.32.

3-Chloro-2-hydroxy-4-aryl-2-cyclobuten-1-ones 8b-q were similarily prepared on a 20 mmol scale. Yields and physical, spectroscopic, and analytical data for the compounds are reported as follows.

3-Chloro-2-hydroxy-4-(*p*-tolyl)-2-cyclobuten-1-one (8b): white crystals; mp 117−118 °C dec (toluene); yield 3.30 g (79%); IR 3160−3140 (s, br), 1740 (vs), 1660 (m) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (s, 3H), 4.45 (s, 1H), 7.15 (d, 2H, J = 8.1 Hz), 7.19 (d, 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 21.18, 61.56, 127.24, 129.64, 130.87, 138.04, 138.27, 148.44, 187.31; MS *m/z* (relative intensity) 210 (M^+, 14), 208 (M^+, 45), 173 (27), 145 (58), 115 (100). Anal. Calcd for $C_{11}H_9ClO_2$: C, 63.32; H, 4.35; Cl, 17.00. Found: C, 62.41; H, 4.46; Cl, 17.21.

3-Chloro-2-hydroxy-4-(4-isopropylphenyl)-2-cyclobuten-1-one (8c): white crystals; mp 88−91 °C dec (toluene); yield 3.65 g (77%); IR 3060−3020 (m, br), 1770 (vs), 1630 (s) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (d, 6H, J = 6.9 Hz), 2.85−2.91 (m, 1H), 4.44 (s, 1H), 7.16 (d, 2H, J = 8.2 Hz), 7.21 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 23.86, 33.83, 61.70, 126.95, 127.19, 131.33, 137.09, 148.35, 149.07, 186.54; MS *m/z* (relative intensity) 238 (M^+, 0.2), 236 (M^+, 0.6), 194 (100), 129 (75). Anal. Calcd for $C_{13}H_{13}ClO_2$: C, 65.97; H, 5.54; Cl, 14.98. Found: C, 65.52; H, 5.41; Cl, 15.21.

4-(4-*tert*-Butylphenyl)-3-chloro-2-hydroxy-2-cyclobuten-1-one (8d): white crystals; mp 149−151 °C dec (CCl_4); yield 3.51 g (70%); IR 3230−3180 (s, br), 1760 (vs), 1665 (s) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, 9H), 4.45 (s, 1H), 7.17 (d, 2H, J = 8.3 Hz), 7.38 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 31.30, 34.61, 61.53, 125.86, 126.97, 130.93, 137.50, 148.37, 151.41, 186.89; MS *m/z* (relative intensity) 252 (M^+, 0.2), 250 (M^+, 0.7), 194 (46), 143 (39), 57 (100). Anal. Calcd for $C_{14}H_{15}ClO_2$: C, 67.07; H, 6.03; Cl, 14.14. Found: C, 66.82; H, 6.00; Cl, 14.58.

3-Chloro-2-hydroxy-4-(4-methoxyphenyl)-2-cyclobuten-1-one (8e): white crystals; mp 111 °C dec (CCl_4); yield 2.12 g (47%); IR 3160−3140 (m, br), 1760 (vs), 1660 (m) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.78 (s, 3H), 4.42 (s, 1H), 6.89 (d, 2H, J = 8.7 Hz), 7.15 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 55.31, 61.38, 114.42, 126.05, 128.40, 137.41, 148.30, 159.72, 186.64; MS *m/z* (relative intensity) 226 (M^+, 13), 224 (M^+, 38), 188 (30), 161 (46), 132 (100). Anal. Calcd for $C_{11}H_9ClO_3$: C, 58.66; H, 4.03; Cl, 15.74. Found: C, 58.57; H, 4.14; Cl, 15.49.

3-Chloro-4-(4-clorophenyl)-2-hydroxy-2-cyclobuten-1-one (8f): white crystals; mp 109−111 °C dec (toluene); yield 4.12 g (90%); IR 3080−3040 (s, br), 1760, 1750 (vs), 1620 (vs) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.44 (s, 1H), 7.17 (dd, 2H, J = 8.5 Hz, J = 1.9 Hz), 7.32 (dd, 2H, J = 8.5 Hz, J = 1.9 Hz); ^{13}C NMR ($CDCl_3$) δ 61.31, 128.58, 129.12, 132.52, 134.34, 136.89, 148.61, 185.87; MS *m/z* (relative intensity) 230 (M^+, 3), 228 (M^+, 4), 193 (60), 165 (63), 136 (100). Anal. Calcd for $C_{10}H_6Cl_2O_2$: C, 52.44; H, 2.64; Cl, 30.95. Found: C, 51.76; H, 2.87; Cl, 31.13.

4-(4-Bromophenyl)-3-chloro-2-hydroxy-2-cyclobuten-1-one (8g): white crystals; mp 117−119 °C dec (toluene); yield 2.57 g (47%); IR 3080−3020 (m, br), 1765 (vs), 1625 (s) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.43 (s, 1H), 7.11 (d, 2H, J = 8.4 Hz), 7.48 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 61.41, 122.42, 128.88, 132.07, 133.03, 136.80, 148.55, 185.53; MS *m/z* (relative intensity) 276 (M^+, 1), 274 (M^+, 5), 272(M^+, 4) 194 (100), 182 (99), 180 (93), 165 (93). Anal. Calcd for $C_{10}H_6BrClO_2$: C, 43.91; H, 2.21; Br, 29.22; Cl, 12.96. Found: C, 43.55; H, 2.24; Br, 29.03; Cl, 12.63.

3-Chloro-2-hydroxy-4-(4-iodophenyl)-2-cyclobuten-1-one (8h): white crystals; mp 127 °C dec (CCl_4); yield 5.13 g (80%); IR 3120−3000 (vs, br), 1770−1730 (vs, br), 1660 (s), 1630-1600 (vs, br), 1580 (s) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.41 (s, 1H), 6.98 (d, 2H, J = 8.4 Hz), 7.68 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 61.62, 93.92, 129.13, 133.81, 136.30, 138.03, 148.69, 185.35; MS *m/z* (relative intensity) 322 (M^+, >1), 320 (M^+, 2), 228(74) 193 (61), 165 (20), 101 (100). Anal. Calcd for $C_{10}H_6ICl O_2$: C, 37.47; H, 1.89; Cl, 11.06; I, 39.59. Found: C, 38.36; H, 1.76; Cl, 11.96; I, 39.51.

3-Chloro-4-(2,4-dimethylphenyl)-2-hydroxy-2-cyclobuten-1-one (8i): white crystals; mp 137−138 °C dec (toluene); yield 2.98 g (67%); IR 3200 (vs, br), 1755 (vs), 1670 (s) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.31 (s, 3H), 2.37 (s, 3H), 4.74 (s, 1H), 7.00−7.08 (m, 3H), 8.93 (s, 1H, OH); ^{13}C NMR ($CDCl_3$) δ 19.44, 21.04, 58.57, 125.82, 126.90, 129.35, 131.60, 136.98,137.71, 137.81, 148.12, 187.96; MS *m/z* (relative intensity) 224 (M^+, 33), 222 (M^+, 99), 187 (54), 159 (90), 115 (100). Anal. Calcd for $C_{12}H_{11}ClO_2$: C, 64.73; H, 4.98; Cl, 15.92. Found: C, 64.33; H, 4.95; Cl, 16.14.

3-Chloro-4-(2,5-dimethylphenyl)-2-hydroxy-2-cyclobuten-1-one (8j): white crystals; mp 138 °C dec (toluene); yield 4.23 g (95%); IR 3160−3160 (vs, br), 1755−1735 (vs,br), 1670 (vs) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (s, 3H), 2.37 (s, 3H), 4.75 (s, 1H), 6.98(s, 1H), 7.03 (d, 1H, J = 8.0Hz), 7.10 (d, 1H, J = 8.0 Hz), 8.99 (s, 1H, OH); ^{13}C NMR ($CDCl_3$) δ 18.97, 20.99, 58.73, 126.43, 128.68, 130.59, 132.03, 133.91, 135.72, 137.56, 148.09, 187.67; MS *m/z* (relative intensity) 224 (M^+, 32), 222 (M^+, 94), 207 (52), 187 (58), 159 (76), 115 (100). Anal. Calcd for $C_{12}H_{11}ClO_2$: C, 64.73; H, 4.98; Cl, 15.92. Found: C, 64.28; H, 4.78; Cl, 16.50.

4-(3,4-Dimethoxyphenyl)-3-chloro-2-hydroxy-2-cyclobuten-1-one (8k): white crystals; mp 111 °C dec (CCl_4); yield 4.53 g (89%); IR 3130−3100 (vs, br), 1760−1740 (vs,br), 1660 (s) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.83 (s, 3H), 3.84 (s, 3H), 4.39 (s, 1H), 6.70 (d, 1H, J = 1.6Hz), 6.78 (dd, 1H, J = 8.2 Hz, J = 1.6 Hz), 6.83 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 56.02, 61.61, 110.51, 111.72, 119.74, 126.62, 137.35, 148.57, 149.14, 149.37, 186.63; MS *m/z* (relative intensity) 256 (M^+, 32), 254 (M^+, 100), 219 (44), 191 (70), 162 (84). Anal. Calcd for $C_{12}H_{11}ClO_4$: C, 56.60; H, 4.35; Cl, 13.92. Found: C, 56.53; H, 4.37; Cl, 14.50.

3-Chloro-4-(2,5-dichlorophenyl)-2-hydroxy-2-cyclobuten-1-one (8m): white crystals; mp 134−136 °C dec (toluene); yield 4.74 g (90%); IR 3160−3140 (s, br), 1755 (vs), 1665 (s) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.01 (s, 1H), 7.18 (d, 1H, J = 2.4 Hz), 7.22 (dd, 1H, J = 8.5 Hz, J = 2.4 Hz), 7.33 (d, 1H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 58.89, 127.68, 129.51, 131.13, 132.72, 133.22, 133.69, 135.89, 148.93, 184.54; MS *m/z* (relative intensity) 264 (M^+, 1), 262 (M^+, 2), 227 (100), 170 (49), 135 (52). Anal. Calcd for $C_{10}H_5Cl_3O_2$: C, 45.58; H, 1.91; Cl, 40.36. Found: C, 45.38; H, 2.00; Cl, 40.38.

3-Chloro-2-hydroxy-4-(2,3,4-trimethylphenyl)-2-cyclobuten-1-one (8n): white crystals; mp 148−149 °C dec (CCl_4); yield 2.13 g (45%); IR 3240 (vs, br), 1760 (vs), 1670 (s) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.19 (s, 3H), 2.26 (s, 3H), 2.29 (s, 3H), 4.81 (s, 1H), 6.94 (d, 1H, J = 7.9 Hz), 6.99 (d, 1H, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$) δ15.71, 20.86, 30.92, 59.36, 122.98, 127.41, 130.21, 135.40, 135.92, 136.35, 136.94, 148.12, 187.24; MS *m/z* (relative intensity) 238 (M^+, 29), 236 (M^+, 88), 221 (100), 173 (54), 144 (62), 129 (88). Anal. Calcd for $C_{13}H_{13}ClO_2$: C, 65.97; H, 5.54; Cl, 14.98. Found: C, 65.50; H, 5.37; Cl, 15.38.

3-Chloro-2-hydroxy-4-mesityl-2-cyclobuten-1-one (8o): white crystals; mp 140 °C dec (toluene); yield 3.27 g (69%); IR

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3200−3140 (vs, br), 1750−1730 (vs,br), 1660 (s), 1600 (m) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3H), 2.30 (s, 6H), 4.94 (s, 1H), 6.83 (s, 2H); ^{13}C NMR ($CDCl_3$) δ20.79, 20.91, 58.15, 126.04, 130.46, 137.73, 137.96, 139.21, 147.52, 189.59; MS *m/z* (relative intensity) 238 (M^+, 20), 236 (M^+, 60), 221 (100), 201 (90), 173 (42), 129 (42). Anal. Calcd for $C_{13}H_{13}ClO_2$: C, 65.97; H, 5.54; Cl, 14.98. Found: C, 66.16; H, 5.45; Cl, 14.25.

3-Chloro-2-hydroxy-4-(2,3,4,5-tetramethylphenyl)-2-cyclobuten-1-one (8p): white crystals; mp 135 °C dec (toluene); yield 4.66 g (93%); IR 3250 (vs, br), 1770 (vs), 1675 (s) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.17 (s, 3H), 2.21 (s, 3H), 2.24 (s, 3H), 2.28 (s, 3H), 4.81 (s, 1H), 6.82 (s, 1H); ^{13}C NMR ($CDCl_3$) δ15.76, 16.10, 16.37, 20.81, 59.31, 124.73, 129.30, 132.84, 133.82, 134.94, 135.90, 137.16, 147.89, 187.31; MS *m/z* (relative intensity) 252 (M^+, 11), 250 (M^+, 33), 235 (100), 207 (36), 158 (23), 143 (30). Anal. Calcd for $C_{14}H_{15}ClO_2$: C, 67.07; H, 6.03; Cl, 14.14. Found: C, 66.07; H, 5.72; Cl, 14.30.

3-Chloro-2-hydroxy-4-(naphthalen-1-yl)-2-cyclobuten-1-one (8q): white crystals; mp 153−156 °C dec (toluene); yield 4.16 g (85%); IR 3140 (s, br), 1745 (vs), 1655 (s) (OH, C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.31 (s, 1H), 7.40−7.58 (m, 4H), 7.80 (d, 1H, J = 7.8 Hz), 7.86 (d, 1H, J = 7.8 Hz), 8.11 (d, 1H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 58.55, 123.31, 123.68, 125.27, 126.14, 126.58, 128.58, 128.66, 130.73, 132.11, 133.84, 136.50, 147.95, 186.27; MS *m/z* (relative intensity) 246 (M^+, 7), 244 (M^+, 22), 181 (22), 152 (100). Anal. Calcd for $C_{14}H_9ClO_2$: C, 68.73; H, 3.71; Cl, 14.50. Found: C, 68.13; H, 3.93; Cl, 15.40.

Reaction of Semisquaric Chloride (7) with 1,4-Dimethoxybenzene (2l) in Dichloromethane at Reflux Temperature. To a solution of semisquaric chloride **(7)** (2.00 g, 17 mmol) and 1,4-dimethoxybenzene **(2l)** (4.75 g, 34 mmol) in dichloromethane (50 mL) was added $AlCl_3$ (4.53 g, 34 mmol) in portions with stirring. The reaction mixture was heated to reflux for 1 h. During this period the color changed from yellow to dark violet. The reaction mixture was poured onto crushed ice (100 g) and the yellow solid which precipitated was collected by filtration. The filtrate was transferred to a separatory funnel and extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, dried ($MgSO_4$), and evaporated to dryness, leaving yellow crystals. The crystal fractions were combined and triturated with boiling ether (100 mL). The yellow crystals left behind were treated with boiling acetone. The major part went into solution and crystallized on cooling to give 3-(2,5-dimethoxyphenyl)-3-cyclobutene-1,2-dione **(9a)**: yellow crystals; mp 195−197 °C (acetone); yield 1.03 g (27%); IR 3100 (w), 2960 (w), 2920 (w), 2820 (w), 1760 (s), 1610 (w), 1540 (m), 1490 (m), 1270 (m), 1250 (m) (C-H, C=O, C=C, C-O-C) cm^{-1}; MS *m/z* (relative intensity) 218 (M^+, 80), 162 (100), 147 (71). Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 65.85; H, 4.48.

The acetone-insoluble residue from above was recrystallized from 1-propanol to give 3,4-bis(2,5-dimethoxyphenyl)-3-cyclobutene-1,2-dione **(10a)**: yellow crystals; mp 228−230 °C (1-propanol); yield 0.48 g (8%); IR 3000 (w), 2960 (w), 2920 (w), 2830 (w), 1775 (s), 1755 (s), 1620 (m), 1500 (m), 1480 (m), 1460 (m) (C−H, C=O, C=C) cm^{-1}. Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.82; H, 5.11.

3-(2,4,5-Trimethoxyphenyl)-3-cyclobutene-1,2-dione (9b). A solution of semisquaric chloride **(7)** (1.16 g, 10 mmol), 1,2,4-trimethoxybenzene **(2r)** (1.68 g, 10 mmol), and trifluoroacetic acid (1 mL) in dichloromethane was stirred at rt for 24 h. During this period the reaction mixture took on a dark green color. The reaction mixture was evaporated *in vacuo* and the remaining residue triturated with hexane (2 × 20 mL). The crystals obtained were recrystallized from acetone with the aid of charcoal to give **9b**: yellow crystals; mp 226−228 °C (acetone); yield 0.52 g (21%); IR 3095 (w), 2980 (w), 2930 (w), 2830 (w), 1765 (s, br), 1610 (m), 1540 (s), 1520 (s), 1450 (m), 1250 (m), 1220 (m) (C−H, C=O, C=C, C−O−C) cm^{-1}; MS *m/z* (relative intensity) 248 (M^+, 49), 192 (100), 177 (45), 149 (19). Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.65; H, 4.87.

Generation of 4-Aryl-3-chloro-2-methoxy-2-cyclobuten-1-ones (Chloroenol Methyl Ethers) 11. General Procedure. The solution of a chloroenol **8** (10 mmol) in diethyl ether (100 mL) was cooled to −15 °C. With stirring, a solution of diazomethane (11.5 mmol) in diethyl ether was added over 5 min, and stirring was continued for further 30 min. Then the solution was carefully evaporated. The remaining yellow oil was submitted to column chromatography, using dichloromethane as the eluent. Exceptionally, **11h** crystallized after removal of the diethyl ether.

3-Chloro-2-methoxy-4-phenyl-2-cyclobuten-1-one (11a): white crystals; mp 36 °C (*n*-hexane); yield 1.54 g (74%); IR 1760 (vs, br), 1635 (s) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.08 (s, 3H), 4.41 (s, 1H), 7.24−7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 58.49, 62.28, 127.29, 128.18, 128.88, 134.36, 134.95, 150.01, 183.15; MS *m/z* (relative intensity) 210 (M^+, 2), 208 (M^+, 7), 165 (22), 137 (31), 102 (100). Anal. Calcd for $C_{11}H_9ClO_2$: C, 63.32; H, 4.35; Cl, 16.99. Found: C, 63.11; H, 4.29; Cl, 17.18.

3-Chloro-2-methoxy-4-(*p*-tolyl)-2-cyclobuten-1-one (11b): white crystals; mp 43−44 °C (*n*-hexane); yield 1.54 g (69%); IR 1780−1750 (vs, br), 1630 (s) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.33 (s, 3H), 4.08 (s, 3H), 4.38 (s, 1H), 7.14 (d, 2H, J = 8.4 Hz), 7.17 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 21.12, 58.41, 62.96, 127.13, 129.53, 131.22, 135.15, 137.94, 149.87, 183.34; MS *m/z* (relative intensity) 224 (M^+, 13), 222 (M^+, 40), 207 (42), 179 (49), 115 (100). Anal. Calcd for $C_{12}H_{11}ClO_2$: C, 64.73; H, 4.98; Cl, 15.92. Found: C, 64.69; H, 5.00; Cl, 16.01.

4-(4-*tert*-Butylphenyl)-3-chloro-2-methoxy-2-cyclobuten-1-one (11c): white crystals; mp 56−57 °C (*n*-hexane); yield 1.61 g (61%); IR 1755 (vs, br), 1635 (s) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, 9H), 4.08 (s, 3H), 4.39 (s, 1H), 7.19 (d, 2H, J = 8.3 Hz), 7.38 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 31.28, 34.55, 58.40, 61.83, 125.75, 126.87, 131.20, 135.09, 149.81, 151.11, 183.36; MS *m/z* (relative intensity) 266 (M^+, 1), 264 (M^+, 4), 208 (97), 193 (47), 115 (26), 57 (100). Anal. Calcd for $C_{15}H_{17}ClO_2$: C, 68.01; H, 6.47; Cl, 13.39. Found: C, 67.90; H, 6.42; Cl, 13.53.

3-Chloro-2-methoxy-4-(4-methoxyphenyl)-2-cyclobuten-1-one (11d): white crystals; mp 48−50 °C (*n*-hexane); yield 1.43 g (60%); IR 1770−1740 (vs, br), 1630 (s), 1605 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.77 (s, 3H), 4.07 (s, 3H), 4.35 (s, 1H), 6.88 (d, 2H, J = 8.7 Hz), 7.16 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 55.29, 58.40, 61.59, 114.35, 126.24, 128.38, 135.37, 149.80, 159.63, 183.60; MS *m/z* (relative intensity) 240 (M^+, 33), 238 (M^+, 98), 223 (61), 195 (100), 175 (70), 132 (96). Anal. Calcd for $C_{12}H_{11}ClO_3$: C, 60.39; H, 4.65; Cl, 14.85. Found: C, 60.45; H, 4.60; Cl, 14.84.

3-Chloro-4-(4-chlorophenyl)-2-methoxy-2-cyclobuten-1-one (11e): white crystals; mp 39−41 °C (*n*-hexane); yield 1.80 g (74%); IR 1755 (vs), 1650 (s) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.05 (s, 3H), 4.37 (s, 1H), 7.17 (d, 2H, J = 8.5 Hz), 7.31 (d, 2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 58.37, 61.49, 128.48, 128.91, 132.79, 133.91, 134.31, 150.01, 182.25; MS *m/z* (relative intensity) 246 (M^+, 1), 244 (M^+, 9), 242 (M^+, 14), 207 (58), 199 (48), 171 (51), 136 (100). Anal. Calcd for $C_{11}H_8Cl_2O_2$: C, 54.35; H, 3.32; Cl, 29.17. Found: C, 54.34; H, 3.36; Cl, 29.20.

3-Chloro-4-(4-iodophenyl)-2-methoxy-2-cyclobuten-1-one (11f): white crystals; mp 59−61 °C (*n*-hexane); yield 2.61 g (78%); IR 1760 (vs, br), 1630 (s) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.06 (s, 3H), 4.34 (s, 1H), 6.99 (d, 2H, J = 8.3 Hz), 7.67 (d, 2H, J = 8.3Hz); ^{13}C NMR ($CDCl_3$) δ 58.56, 61.86, 93.71, 129.16, 134.15, 134.38, 138.00, 150.24, 182.20; MS *m/z* (relative intensity) 336 (M^+, 2), 334 (M^+, 6), 207 (78), 164 (100), 136 (39), 101 (61). Anal. Calcd for $C_{11}H_8ClIO_2$: C, 39.49; H, 2.41; Cl, 10.60; I, 37.93. Found: C, 40.04; H, 2.55; Cl, 10.77; I, 37.46.

3-Chloro-4-(2,5-dimethoxyphenyl)-2-methoxy-2-cyclobuten-1-one (11g): white crystals; mp 59−61 °C (*n*-hexane); yield 1.88 g (70%); IR 1755 (vs, br), 1640 (s), 1605 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.73 (s, 3H), 3.76 (s, 3H), 4.05 (s, 3H), 4.81 (s, 1H), 6.70 (d, 1H, J = 2.9 Hz), 6.76 (dd, 1H, J = 8.9 Hz, J = 2.9 Hz), 6.81 (d, 1H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 55.71, 56.55, 56.91, 58.32, 112.55, 113.33, 114.03, 123.89, 134.60, 149.66, 152.60, 153.78, 183.48; MS *m/z* (relative intensity) 270 (M^+, 22), 238 (M^+, 80), 249 (76), 210 (100), 191 (46), 121 (56). Anal. Calcd for $C_{13}H_{13}ClO_4$: C, 58.11; H, 4.88; Cl, 13.19. Found: C, 58.06; H, 4.79; Cl, 13.25.

3-Chloro-4-(2,5-dichlorophenyl)-2-methoxy-2-cyclobuten-1-one (11h): white crystals; mp 96−97 °C (EtOAc); yield 2.39 g (86%); IR 1770 (vs, br), 1635 (s) (C=O, C=C) cm^{-1};

^{1}H NMR ($CDCl_3$) δ 4.08 (s, 3H), 4.93 (s, 1H), 7.17−7.31 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 58.54, 59.15, 127.53, 129.22, 131.03, 132.71, 133.03, 133.29, 134.01, 150.46, 180.95; MS *m/z* (relative intensity) 278 (M^+, 3), 276 (M^+, 3), 241 (81), 205 (47), 170 (100), 99 (44). Anal. Calcd for $C_{11}H_7Cl_3O_2$: C, 47.61; H, 2.54; Cl, 38.32. Found: C, 47.69; H, 2.63; Cl, 38.05.

3-Chloro-2-methoxy-4-(2,3,4,5-tetramethylphenyl)-2-cyclobuten-1-one (11i): white crystals; mp 81 °C (*n*-hexane); yield 0.93 g (35%); IR 1750 (vs), 1645 (m), (C=O, C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3H), 2.22 (s, 3H), 2.26 (s, 3H), 2.30 (s, 3H), 4.08 (s, 3H), 4.77 (s, 1H), 6.85 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 15.74, 16.07, 16.35, 20.82, 58.35, 59.52, 124.57, 129.50, 132.87, 133.67, 134.70, 135.21, 135.81, 149,37 184.16; MS *m/z* (relative intensity) 266 (M^+, 23), 264 (M^+, 68), 249 (100), 221 (40), 201 (32), 143 (47). Anal. Calcd for $C_{15}H_{17}ClO_4$: C, 68.05; H, 6.47; Cl, 13.39. Found: C, 68.06; H, 6.41; Cl, 13.25.

3-Chloro-2-methoxy-4-(naphthalen-1-yl)-2-cyclobuten-1-one (11j): white crystals; mp 82−83 °C (*n*-hexane); yield 1.37 g (53%); IR 1750 (vs), 1640 (s) (C=O, C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.10 (s, 3H), 5.26 (s, 1H), 7.44−7.59 (m, 4H), 7.79−7.87 (m, 2H), 8.15 (d, 1H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 58.49, 58.78, 123.48, 125.26, 126.09, 126.52, 128.40, 128.61, 131.08, 132.21, 133.85, 134.29, 149.51, 183.09; MS *m/z* (relative intensity) 260 (M^+, 4), 258 (M^+, 12), 242 (58), 214 (47), 152 (100). Anal. Calcd for $C_{15}H_{11}ClO_2$: C, 69.64; H, 4.29; Cl, 13.70. Found: C, 69.31; H, 4.30; Cl, 13.60.

Generation of 4-Aryl-3-chloro-2-cyclobutene-1,2-diones. General Procedure. Chlorine was introduced into a magnetically stirred suspension of a chloroenol **8** (10 mmol) in tetrachloromethane (100 mL). After ca. 15 min the suspension had turned into a clear orange solution. This solution was heated to reflux for 30 min, and the solvent then was removed *in vacuo*, leaving a solid behind.

3-Chloro-4-phenyl-3-cyclobutene-1,2-dione (12a): yellow crystals; mp 113−114 °C (CCl_4/*n*-hexane), (lit.[10] mp 114−115 °C); yield 1.52 g (79%). Anal Calcd for $C_{10}H_5ClO_2$: C, 62.36; H, 2.62; Cl, 18.41. Found: C, 62.19; H, 2.71; Cl, 18.19.

3-Chloro-4-(*p*-tolyl)-3-cyclobutene-1,2-dione (12b): yellow crystals; mp 136−137 °C (CCl_4/*n*-hexane); yield 1.03 g (50%); IR 1800 (s), 1780−1760 (vs, br), 1600 (m) (C=O, C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3H), 7.35 (d, 2H, J = 8.0 Hz), 8.08 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 22.19, 124.19, 128.94, 130.35, 146.79, 179.05, 188.80, 190.77, 194.52; MS *m/z* (relative intensity) 208 (M^+, 7), 206 (M^+, 23), 150 (91), 143 (51), 115 (100). Anal. Calcd for $C_{11}H_7ClO_2$: C, 63.94; H, 3.41; Cl, 17.16. Found: C, 63.94; H, 3.66; Cl, 16.74.

4-(4-*tert*-Butylphenyl)-3-chloro-3-cyclobutene-1,2-dione (12c): yellow crystals; mp 92−93 °C (*i*-Pr_2O); yield 1.94 g (78%); IR 1800 (s), 1760−1720 (vs, br), 1610 (m) (C=O, C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 9H), 7.59 (dd, 2H, J = 6.7 Hz, J = 1.9 Hz), 8.17 (dd, 2H, J = 6.7 Hz, J = 1.9 Hz); ^{13}C NMR ($CDCl_3$) δ 30.84, 35.55, 124.07, 126.54, 128.83, 159.51, 179.16, 188.82, 190.78, 194.45; MS *m/z* (relative intensity) 250 (M^+, 3), 248 (M^+, 9), 192 (58), 177 (100). Anal. Calcd for $C_{14}H_{13}ClO_2$: C, 67.61; H, 5.27; Cl, 14.25. Found: C, 67.21; H, 5.19; Cl, 14.59.

3-Chloro-4-(4-methoxyphenyl)-3-cyclobutene-1,2-dione (12d): yellow crystals; mp 119−121 °C (CCl_4), (lit.[11] mp 122−123 °C); yield 1.47 g (66%); IR 1800 (m), 1785, 1760 (vs, br), 1590 (m) (C=O, C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.90 (s, 3H), 7.04 (dd, 2H, J = 7.0 Hz, J = 2.0 Hz), 8.20 (dd, 2H, J = 7.0 Hz, J = 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 55.68, 115.13, 119.62, 131.35, 165.15, 176.86, 187.71, 190.37, 194.74; MS *m/z* (relative intensity) 224 (M^+, 19), 222 (M^+, 57), 166 (100), 159 (49), 123 (46). Anal. Calcd for $C_{11}H_7ClO_3$: C, 59.35; H, 3.17; Cl, 15.92. Found: C, 58.18; H, 3.43; Cl, 17.88.

3-Chloro-4-(4-chlorophenyl)-3-cyclobutene-1,2-dione (12e): yellow crystals; mp 139−140 °C (CCl_4/*n*-hexane), (lit.[11] mp 142−142.5 °C; yield 1.45 g (64%); IR 1765 (vs, br), 1585 (m) (C=O, C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.55 (dd, 2H, J = 6.7 Hz, J = 1.9 Hz), 8.17 (dd, 2H, J = 6.7 Hz, J = 1.9 Hz); ^{13}C NMR ($CDCl_3$) δ 125.16, 130.04, 130.15, 141.70, 180.63, 187.27, 190.40, 193.99; MS *m/z* (relative intensity) 230 (M^+, 3), 228 (M^+, 19), 226 (M^+, 29), 170 (100), 163 (36). Anal. Calcd for $C_{10}H_4Cl_2O_2$: C, 52.90; H, 1.78; Cl, 31.23. Found: C, 52.77; H, 1.92; Cl, 31.86.

3-Chloro-4-(2,5-dimethylphenyl)-3-cyclobutene-1,2-dione (12f): yellow crystals; mp 64 °C (*i*-Pr_2O); yield 1.24 g (56%); IR 1790−1775 (vs), 1560 (w) (C=O, C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3H), 2.46 (s, 3H), 7.24 (d, 1H, J = 7.9 Hz), 7.29 (d, 1H, J = 7.9 Hz), 7.49 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 20.64, 20.85, 125.79, 128.87, 131.60, 134.30, 135.64, 135.88, 182.68, 191.51, 193.52, 195.50; MS *m/z* (relative intensity) 222 (M^+, 23), 220 (M^+, 69), 164 (100), 157 (49), 129 (95). Anal. Calcd for $C_{12}H_9ClO_2$: C, 65.32; H, 4.11; Cl, 16.07. Found: C, 64.98; H, 4.46; Cl, 16.16.

3-Chloro-4-(2-chloro-4,5-dimethoxyphenyl)-3-cyclobutene-1,2-dione (12g): obtained from the chlorination of **8k**; yellow crystals; mp 128 °C (CCl_4/*n*-hexane); yield 2.12 g (74%); IR 1810 (s), 1785−1755 (vs,br), 1585 (s) (C=O, C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 3H), 3.95 (s, 3H), 7.01 (s, 1H), 7.38 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 56.39, 56.51, 111.74, 113.74, 117.80, 127.67, 148.02, 154.02, 181.74, 190.22, 191.55, 193.20; MS *m/z* (relative intensity) 290 (M^+, 4), 288 (M^+, 28), 286 (M^+, 43), 230 (100), 152 (21). Anal. Calcd for $C_{12}H_8Cl_2O_4$: C, 50.20; H, 2.81; Cl, 24.70. Found: C, 50.20; H, 3.14; Cl, 24.26.

Generation of 3-Aryl-4-methoxy-3-cyclobutene-1,2-diones 13. General Procedure. To the solution of a chloroenol **8** (5 mmol) in MeOH (25 mL) was added bromine 0.80 g (5 mmol). When the reaction mixture was shaken vigorously the product started to precipitate from the solution. After 5 min of shaking the suspension was cooled to −15 °C. The precipitate was collected by filtration.

3-Methoxy-4-phenyl-3-cyclobutene-1,2-dione (13a): yellow crystals; mp 148−150 °C (MeOH), (lit.[10] mp 151−152 °C); yield 1.05 g (56%); IR 1780−1770 (vs, br), 1740−1720 (vs, br), 1590−1570 (vs, br) (C=O, C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.56 (s, 3H), 7.44−7.50 (m, 3H), 7.97−8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 61.71, 127.61, 127.74, 129.10, 132.74, 173.73, 192.33, 192.70, 194.84; MS *m/z* (relative intensity) 188 (M^+, 24), 145 (48), 132 (29), 117 (35), 89 (100). Anal. Calcd for $C_{11}H_8O_3$: C, 70.21; H, 4.29. Found: C, 69.88; H, 4.38.

3-Methoxy-4-(*p*-tolyl)-3-cyclobutene-1,2-dione (13b): yellow crystals; mp 160 °C (MeOH); yield 1.42 g (70%); IR 1780, 1780−1730 (vs, br), 1590 (vs) (C=O, C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3H), 4.53 (s, 3H), 7.24 (d, 2H, J = 7.9 Hz), 7.85 (d, 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 21.90, 61.58, 124.96, 127.77, 129.84, 143.86, 173.76, 192.04, 192.91, 194.29; MS *m/z* (relative intensity) 202 (M^+, 40) 159 (44), 146 (67), 131 (81), 103 (100). Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.06; H, 4.97.

4-(4-Chlorophenyl)-3-methoxy-3-cyclobutene-1,2-dione (13c): yellow crystals; mp 129−130 °C (MeOH); yield 1.14 g (51%); IR 1780, 1750−1730 (vs, br), 1580 (vs, br) (C=O, C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.57 (s, 3H), 7.44 (d, 2H, J = 8.5 Hz), 7.92 (d, 2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 61.87, 125.95, 128.86, 129.55, 138.97, 172.20, 192.00, 192.28, 194.79; MS *m/z* (relative intensity) 224 (M^+, 10), 222 (M^+, 30) 166 (59), 152 (67), 123 (100). Anal. Calcd for $C_{11}H_7ClO_3$: C, 59.35; H, 3.17; Cl, 15.92. Found: C, 59.19; H, 3.04; Cl, 16.04.

Generation of 3-Aryl-3-cyclobutene-1,2-diones 14. Method A. A solution of a chloroenol **8** (40 mg) in DMSO-d_6 (2.5 mL) was kept at rt for 24 h and was then submitted to NMR spectroscopy.

Method B. A solution of 3-chloro-2-hydroxy-4-phenyl-2-cyclobuten-1-one **(8a)** (1.96g, 10 mmol) in DMSO (50 mL) was kept at rt for 24 h. The solution was then poured onto an ice−water mixture (100 g). The precipitate was collected by filtration and recrystallized from acetone.

Method C. A solution of a chloroenol **8** (10 mmol) in a mixture of acetone/H_2O (30 mL; 3:2 vol:vol) was heated with stirring to reflux for 1 h. During this period the product started to crystallize. The reaction mixture was cooled in an ice bath and the product collected by filtration.

3-Phenyl-3-cyclobutene-1,2-dione (14a). Method A and Method B: yellow crystals; mp 149−150 °C (acetone), (lit.[10] mp 152−153 °C); yield 0.32 g (38%). IR 1765 (vs, br), 1590 (m) (C=O, C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.60−7.70 (m, 3H), 7.80−8.02 (m, 2H), 10.11 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 127.36, 128.99, 129.43, 134.18, 180.61, 194.57, 196.10, 198.24; MS *m/z* (relative intensity) 158 (M^+, 17), 102 (100), 91 (12), 76 (27). Anal. Calcd for $C_{10}H_6O_2$: C, 75.94; H, 3.82. Found: C, 75.75; H, 3.79.

3-(*p*-Tolyl)-3-cyclobutene-1,2-dione (14b). Method C: yellow crystals; mp 158−160 °C dec (acetone), (lit.[24] mp 166 °C); yield 1.00 g (58%); IR 1765 (vs, br), 1600 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.43 (s, 3H), 7.34 (d, 2H, J = 8.1 Hz), 7.86 (d, 2H, J = 8.1 Hz), 9.45 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.07, 124.79, 129.50, 130.35, 146.17, 177.14, 195.44, 195.75, 198.06; MS *m/z* (relative intensity) 172 (M^+, 18), 116 (100), 89 (11). Anal. Calcd for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.50; H, 4.69.

3-(4-Isopropylphenyl)-3-cyclobutene-1,2-dione (14c). Method A: ^1H NMR (DMSO-d_6) δ 1.22 (d, 6H, J = 6.9 Hz), 2.98 (m, 1H), 7.52 (d, 2H, J = 8.1 Hz), 7.96 (d, 2H, J = 8.2 Hz), 10.08 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 23.29, 33.73, 125.19, 127.53, 129.29, 155.65, 179.85, 194.42, 196.12, 198.54.

3-(4-*tert*-Butylphenyl)-3-cyclobutene-1,2-dione (14d). Method C: yellow crystals; mp 163−164 °C (acetone); yield 1.35 g (63%); IR 1775 (vs), 1600 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (s, 9H), 7.56 (d, 2H, J = 8.3 Hz), 7.91 (d, 2H, J = 8.3 Hz), 9.48 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 30.89, 35.44, 124.59, 126.52, 129.31, 158.98, 177.15, 195.20, 195.66, 197.96; MS *m/z* (relative intensity) 214 (M^+, 34), 158 (41), 143 (100), 115 (32). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.05; H, 6.76.

3-(4-Methoxyphenyl)-3-cyclobutene-1,2-dione (14e). Method C: yellow crystals; mp 156−158 °C dec (acetone), (lit.[6a] 159−162 °C dec); yield 1.07 g (57%); IR 1755 (vs, br), 1595 (s) (C=O, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.87 (s, 3H), 7.20 (d, 2H, J = 8.8 Hz), 8.02 (d, 2H, J = 8.8 Hz), 9.96 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 55.72, 115.12, 120.07, 131.48, 164.12, 178.00, 193.48, 195.65, 198.81; MS *m/z* (relative intensity) 188 (M^+, 26), 132 (100), 117 (31), 89 (41). Anal. Calcd for $C_{11}H_8O_3$: C, 70.21; H, 4.29. Found: C, 70.29; H, 4.39.

3-(4-Chlorophenyl)-3-cyclobutene-1,2-dione (14f). Method C: yellow crystals; mp 179−181 °C dec (acetone), (lit.[24] mp 182 °C); yield 1.28 g (66%); IR 1765 (vs, br), 1585 (m) (C=O, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.73 (d, 2H, J = 8.0 Hz), 8.05 (d, 2H, J = 8.0 Hz), 10.16 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 126.19, 129.74, 130.66, 138.91, 181.02, 193.16, 195.97, 197.88; MS *m/z* (relative intensity) 194 (M^+, 13), 192 (M^+, 39), 136 (100), 101 (48). Anal. Calcd for $C_{10}H_5ClO_2$: C, 62.36; H, 2.62; Cl, 18.41. Found: C, 62.24; H, 2.61; Cl, 18.15.

3-(4-Bromophenyl)-3-cyclobutene-1,2-dione (14g). Method C: yellow crystals; mp 183−185 °C dec (acetone), (lit.[24] mp 190 °C); yield 1.33 g (56%); IR 1765 (vs, br), 1585 (m) (C=O, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.88 (d, 2H, J = 8.4 Hz), 7.95 (d, 2H, J = 8.4 Hz), 10.14 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 126.47, 128.10, 130.65, 132.68, 180.97, 193.28, 195.96, 197.84; MS *m/z* (relative intensity) 182 (M^+, 78), 180 (M^+, 81), 101 (100), 75 (85). Anal. Calcd for $C_{10}H_5BrO_2$: C, 50.67; H, 2.13; Br, 33.71. Found: C, 50.68; H, 1.92; Cl, 31.33.

3-(2,4-Dimethylphenyl)-3-cyclobutene-1,2-dione (14h). Method A: ^1H NMR (DMSO-d_6) δ 2.34 (s, 3H), 2.44 (s, 3H), 7.24 (d, 1H, J = 8.0 Hz), 7.27 (s, 1H), 8.08 (d, 1H, J = 7.9 Hz), 9.85 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 20.98, 21.23, 124.37, 127.06, 129.54, 132.25, 139.95, 144.75, 180.57, 192.81, 196.73, 199.20.

3-(2,5-Dimethylphenyl)-3-cyclobutene-1,2-dione (14i). Method C: yellow crystals; mp 151−152 °C (acetone); yield 1.28 g (69%); IR 1775−1755 (vs, br), 1605 (w) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.37 (s, 3H), 2.46 (s, 3H), 7.24 (d, 1H, J = 7.8 Hz), 7.32 (d, 1H, J = 7.8 Hz), 8.16 (s, 1H), 9.38 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 20.64, 21.24, 126.81, 130.83, 131.52, 135.10, 136.52, 136.75, 179.22, 194.80, 196.20, 198.50; MS *m/z* (relative intensity) 186 (M^+, 37), 130 (100), 115 (72). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.02; H, 5.64.

3-(2,5-Dimethoxyphenyl)-3-cyclobutene-1,2-dione (14j). Method C: yellow crystals; mp 196−197 °C dec (acetone); yield 1.13 g (52%); IR 1760 (vs), 1610 (w) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.83 (s, 3H), 3.94 (s, 3H), 6.95 (d, 1H, J = 9.2 Hz), 7.17 (dd, 1H, J = 9.2 Hz, J = 3.2 Hz), 7.88 (d, 1H, J = 3.2 Hz), 9.52 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 56.03, 112.14, 113.79, 117.02, 123.29, 153.57, 153.62, 180.90, 190.81, 197.06, 199.22; MS *m/z* (relative intensity) 218 (M^+, 73), 162 (100), 147 (86), 119 (20). Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 65.87; H, 4.72.

3-(2,5-Dichlorophenyl)-3-cyclobutene-1,2-dione (14k). Method C: yellow crystals; mp 182 °C dec (acetone); yield 1.50 g (66%); IR 1775 (vs, br), 1580 (w) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.52 (d, 2H, J = 1.4 Hz), 8.42 (t, 1H, J = 1.4 Hz), 9.88 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 127.19, 130.95, 132.11, 133.74, 133.96, 134.56, 182.47, 190.56, 195.52, 196.93; MS *m/z* (relative intensity) 230 (M^+, >1), 228 (M^+, 2), 226 (M^+, 3), 170 (100), 135 (20), 99 (42). Anal. Calcd for $C_{10}H_4Cl_2O_2$: C, 52.90; H, 1.78; Cl, 31.23. Found: C, 52.81; H, 1.73; Cl, 31.15.

3-(2,3,4-Trimethylphenyl)-3-cyclobutene-1,2-dione (14l). Method A: ^1H NMR (DMSO-d_6) δ 2.22 (s, 3H), 2.32 (s, 3H), 2.37 (s, 3H), 7.23 (d, 1H, J = 7.9 Hz), 7.87 (d, 1H, J = 7.9 Hz), 9.87 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 15.50, 17.13, 21.09, 125.37, 126.78, 127.62, 136.58, 137.74, 143.20, 181.00, 194.45, 196.67, 199.17.

3-(2,3,4,5-Tetramethylphenyl)-3-cyclobutene-1,2-dione (14m). Method A: ^1H NMR (DMSO-d_6) δ 2.19 (s, 3H), 2.20 (s, 3H), 2.23 (s, 3H), 2.30 (s, 3H), 7.72 (s, 1H), 9.80 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 15.98, 16.61, 17.17, 20.11, 124.69, 127.91, 133.75, 135.23, 136.43, 141.93, 180.86, 194.54, 196.60, 199.07.

3-(Naphthalen-1-yl)-3-cyclobutene-1,2-dione (14n). Method C: orange crystals; mp 143 °C (acetone); yield 0.89 g (43%); IR 1760 (vs, br), 1570 (w) (C=O, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.65−7.74 (m, 3H), 8.08 (d, 1H, J = 9.3 Hz), 8.26 (d, 1H, J = 8.2 Hz), 8.37−8.42 (m, 2H), 10.36 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 124.10, 124.52, 125.41, 127.00, 128.53, 129.18, 129.59, 129.86, 133.31, 134.92, 181.39, 192.68, 196.67, 198.78; MS *m/z* (relative intensity) 208 (M^+, 1), 180 (12), 152 (100). Anal. Calcd for $C_{14}H_8O_2$: C, 80.76; H, 3.87. Found: C, 80.75; H, 3.74.

Generation of 4-Aryl-3-cyclobutene-1,2-diones-3-*d* 15. General Procedures. Variant A. To the solution of either chloroenol **8a** or **8f** (3 mmol) in a mixture of acetone-d_6/D_2O (10 mL; 3:2 vol:vol) was added DCl (36% in D_2O; 3 drops). The mixture was heated with stirring to reflux for 1 h. During this period the product started to crystallize. The reaction mixture was cooled in an ice bath and the product collected by filtration. Variant B. For the substrates **8b** and **8d**: As Variant A but without the addition of DCl.

4-Phenyl-3-cyclobutene-1,2-dione-3-*d* (15a). Variant A: yellow crystals; mp 151 °C (EtOH); yield 0.23 g (49%); IR 1785−1760 (vs, br), 1590 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53−7.65 (m, 3H), 7.98−7.99 (m, 2H), 9.54 (s, 0.13H); MS *m/z* (relative intensity) 159 (M^+, 13), 103 (100). Anal. Calcd for $C_{10}H_5DO_2$: C, 75.47; H/D, 4.43. Found: C, 75.09; H/D, 4.22.

4-(*p*-Tolyl)-3-cyclobutene-1,2-dione-3-*d* (15b). Variant B: yellow crystals; mp 162−163 °C (acetone); yield 0.22 g (43%); IR 1765 (vs, br), 1600 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.44 (s, 3H), 7.35 (d, 2H, J = 7.9 Hz), 7.87 (d, 2H, J = 8.1 Hz), 9.46 (s, 0.25H); MS *m/z* (relative intensity) 173 (M^+, 6), 116 (100). Anal. Calcd for $C_{11}H_7DO_2$: C, 76.29; H/D, 5.24. Found: C, 76.20; H/D, 5.29.

4-(4-*tert*-Butylphenyl)-3-cyclobutene-1,2-dione-3-*d* (15c). Variant B: yellow crystals; mp 165 °C dec (acetone); yield 0.33 g (51%); IR 1775(vs), 1600 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (s, 9H), 7.55 (d, 2H, J = 8.1 Hz), 7.91 (d, 2H, J = 8.2 Hz), 9.48 (s, 0.25H); MS *m/z* (relative intensity) 215 (M^+, 4), 144 (100), 128 (17), 116 (38). Anal. Calcd for $C_{14}H_{13}DO_2$: C, 78.11; H/D, 7.02. Found: C, 78.23; H/D, 6.91.

4-(4-Chlorophenyl)-3-cyclobutene-1,2-dione-3-*d* (15d). Variant A: yellow crystals; mp 183 °C dec (EtOH); yield 0.33 g (57%); IR 1765 (vs), 1590 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.54 (d, 2H, J = 8.4 Hz), 7.93 (d, 2H, J = 8.4 Hz), 9.52 (s, 0.05H); MS *m/z* (relative intensity) 196 (M^+, 6), 194 (M^+, 17), 138 (100), 102 (12), 75 (14). Anal. Calcd for $C_{10}H_4ClDO_2$: C, 62.04; H/D, 3.12. Found: C, 62.01; H/D 2.93.

Thermal Isomerization of 4-Aryl-3-chloro-2-hydroxy-2-cyclobuten-1-ones 8. Generation of 3-Chloronaphthalene-1,2-diols 17. General Procedures. Variant A (for the isomerization of **8a** and **8i**). A suspension of either chloroenol **8a** or **8i** (10 mmol) in *m*-xylene (30 mL) was purged with nitrogen and heated with stirring to 139 °C for 3 h. The

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solvent was removed *in vacuo* to give a brown oil. This oil was extracted with hot hexane (6 × 15 mL). On cooling the combined hexane fractions, the products crystallized and were collected by filtration. Variant B: As described in variant A with the difference that the xylene reaction solutions were cooled to −15 °C. The products then crystallized and were collected by filtration.

3-Chloronaphthalene-1,2-diol (17a). Variant A: white crystals; mp 112−114 °C (*n*-hexane), (lit.[20] mp 116−117 °C); yield 1.60 g (82%). IR 3400−3350 (vs, br), 1590 (m) (OH, C=C) cm^{-1}; MS *m/z* (relative intensity) 196 (M^+, 33), 194 (M^+, 100), 131 (34), 113 (15), 102 (50). Anal. Calcd for $C_{10}H_7ClO_2$: C, 63.32; H, 4.35; Cl, 17.00. Found: C, 63.37; H, 4.31; Cl, 16.57.

3-Chloro-7-methylnaphthalene-1,2-diol (17b). Variant B: white crystals; mp 160−162 °C (*n*-hexane); yield 1.67 g (80%); IR 3400−3340 (vs, br), 1600 (m) (OH, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.42 (s, 3H), 7.15 (dd, 1H, J = 8.3 Hz, J = 1.4 Hz), 7.45 (s, 1H), 7.60 (d, 1H, J = 8.3 Hz), 7.80 (s, 1H), 9.25 (s, 2H, OH); ^{13}C NMR (DMSO-d_6) δ 21.52, 118.23, 119.94, 122.53, 124.78, 126.35, 126.46, 126.59, 134.15, 136.95, 139.44; MS *m/z* (relative intensity) 210 (M^+, 73), 208 (M^+, 100), 173 (66), 145 (68), 115 (73). Anal. Calcd for $C_{11}H_9ClO_2$: C, 63.32; H, 4.35; Cl, 17.00. Found: C, 63.37; H, 4.31; Cl, 16.57.

3,7-Dichloronaphthalene-1,2-diol (17d). Variant B: pale red crystals; mp 172−173 °C (toluene); yield 1.63 g (71%); IR 3500, 3420 (vs, br), 1590 (m) (OH, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.31 (dd, 1H, J = 8.8 Hz, J = 2.1 Hz), 7.58 (s, 1H), 7.76 (d, 1H, J = 8.8 Hz), 8.00 (s, 1H), 9.51 (s, 1H, OH), 9.64 (s, 1H, OH); ^{13}C NMR (DMSO-d_6) δ 118.75, 119.80, 124.00, 124.60, 125.32, 126.15, 129.05, 129.94, 138.26, 139.10; MS *m/z* (relative intensity) 232 (M^+, 26), 230 (M^+, 92), 228 (M^+, 100), 193 (66), 165 (51), 136 (64). Anal. Calcd for $C_{10}H_6Cl_2O_2$: C, 52.44; H, 2.64; Cl, 30.95. Found: C, 52.36; H, 2.78; Cl, 30.84.

3-Chloro-7-iodonaphthalene-1,2-diol (17e). Variant B: pale red crystals; mp 148 °C (toluene); yield 2.12 g (66%); IR 3420-3360 (vs, br), 1580 (m) (OH, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.51−7.57 (m, 3H), 8.38 (s, 1H), 9.54 (s, 2H, OH); ^{13}C NMR (DMSO-d_6) δ 91.07, 118.69, 124.22, 126.21, 126.36, 128.70, 129.50, 132.15, 137.98, 138.76; MS *m/z* (relative intensity) 322 (M^+, 32), 320 (M^+, 100), 165 (13), 101 (30). Anal. Calcd for $C_{10}H_6ICl O_2$: C, 37.47; H, 1.89; Cl, 11.06; I, 39.59. Found: C, 37.95; H, 1.95; Cl, 11.53; I, 39.02.

3-Chloro-5,8-dimethylnaphthalene-1,2-diol (17f). Variant A: white crystals; mp 95−96 °C (*n*-hexane); yield 1.25 g (56%); IR 3480, 3400 (s, br), 1585 (w) (OH, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.46 (s, 3H), 2.79 (s, 3H), 6.97 (d, 1H, J = 7.1 Hz), 7.01 (d, 1H, J = 7.1 Hz), 7.43 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 19.35, 24.32, 115.01, 122.86, 123.86, 124.95, 127.33, 128.62, 130.38, 131.75, 137.13, 143.89; MS *m/z* (relative intensity) 224 (M^+, 76), 222 (M^+, 100), 207 (72), 187 (58), 128 (67), 159 (36), 115 (68). Anal. Calcd for $C_{12}H_{11}ClO_2$: C, 64.73; H, 4.98; Cl, 15.92. Found: C, 64.69; H, 4.87; Cl, 16.03.

3,5,8-Trichloronaphthalene-1,2-diol (17g). Variant B: red crystals; mp 166−167 °C (toluene); yield 2.08 g (79%); IR 3500, 3450 (s), 1585 (w) (OH, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.38 (d, 1H, J = 8.0 Hz), 7.41 (d, 1H, J = 8.0 Hz), 7.73 (s, 1H), 9.72 (s, 2H, OH); ^{13}C NMR (DMSO-d_6) δ 115.17, 122.10, 124.41, 125.52, 126.21, 127.20, 127.88, 128.56, 140.31, 141.99; MS *m/z* (relative intensity) 268 (M^+, 4), 266 (M^+, 31), 264 (M^+, 98), 262 (M^+, 100), 163 (21), 135 (19). Anal. Calcd for $C_{10}H_5Cl_3O_2$: C, 45.58; H, 1.91; Cl, 40.36. Found: C, 45.38; H, 2.00; Cl, 40.38.

3-Chlorophenanthrene-1,2-diol (17h). Variant B: grey powder; mp 168−170 °C (toluene); yield 1.57 g (64%); IR 3500 (s), 3360−3320 (s, br), 1610 (w), 1595 (w) (OH, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.52−7.62 (m, 2H), 7.72 (d, 1H, J = 9.2 Hz), 7.89 (d, 1H, J = 7.7 Hz), 8.02 (d, 1H, J = 9.1 Hz), 8.34 (s, 1H), 8.65 (d, 1H, J = 8.2 Hz), 9.47 (s, 1H, OH), 9.58 (s, 1H, OH); ^{13}C NMR (DMSO-d_6) δ 114.30, 120.08, 122.07, 122.68, 122.88, 123.92, 125.70, 126.09, 126.80, 128.28, 129.01, 130.71, 138.74, 141.42; MS *m/z* (relative intensity) 246 (M^+, 31), 244 (M^+, 100), 181 (28), 152 (32). Anal. Calcd for $C_{14}H_9ClO_2$: C, 68.73; H, 3.71; Cl, 14.50. Found: C, 68.73; H, 3.71; Cl, 14.22.

Thermal Isomerization of 4-Aryl-3-chloro-2-methoxy-2-cyclobuten-1-ones 11. Generation of 3-Chloro-2-methoxy-1-naphthols 18. General Procedure. The solution of a 4-aryl-3-chloro-2-methoxy-2-cyclobuten-1-one (chloroenol methyl ether) **11** (5 mmol) in *m*-xylene (20 mL) was purged with nitrogen and heated with stirring to 139 °C for 3 h. The solvent was removed *in vacuo* to give a solid, which was recrystallized from *n*-hexane or toluene.

3-Chloro-2-methoxy-1-naphthol (18a): white crystals; mp 80−81 °C (*n*-hexane); yield 1.34 g (64%); IR 3380 (vs, br), 1585 (m) (OH, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.80 (s, 3H), 7.43−7.46 (m, 2H), 7.53 (s, 1H), 7.75−7.77 (m, 1H), 8.09−8.11 (m, 1H), 10.07 (s, 1H, OH); ^{13}C NMR (DMSO-d_6) δ 60.78, 118.24, 121.84, 124.60, 125.10, 126.10, 126.55, 126.64, 130.49, 138.35, 145.57; MS *m/z* (relative intensity) 210 (M^+, 30), 208 (M^+, 93), 193 (100), 165 (28), 101 (55). Anal. Calcd for $C_{11}H_9ClO_2$: C, 63.32; H, 4.35; Cl, 16.99. Found: C, 63.14; H, 4.34; Cl, 16.66.

3-Chloro-2-methoxy-7-methyl-1-naphthol (18b): white crystals; mp 84−86 °C (*n*-hexane); yield 1.93 g (81%); IR 3480−3440 (s, br), 1595 (m) (OH, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.44 (s, 3H), 3.78 (s, 3H), 7.27 (dd, 1H, J = 8.4 Hz, J = 1.6 Hz), 7.46 (s, 1H), 7.65 (d, 1H, J = 8.4 Hz), 7.87 (s, 1H), 9.94 (s, 1H, OH); ^{13}C NMR (DMSO-d_6) δ 21.33, 60.75, 118.02, 120.73, 124.72, 125.56, 126.48, 128.25, 128.78, 134.43, 138.40, 145.04; MS *m/z* (relative intensity) 224 (M^+, 32), 222 (M^+, 98), 207 (100), 179 (25), 115 (47). Anal. Calcd for $C_{12}H_{11}ClO_2$: C, 64.73; H, 4.98; Cl, 15.92. Found: C, 64.62; H, 5.03; Cl, 16.10.

7-(*tert*-Butyl)-3-chloro-2-methoxy-1-naphthol (18c): white crystals; mp 84−85 °C (*n*-hexane); yield 1.99 g (75%); IR 3490 (s, br), 1590 (w) (OH, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.33 (s, 9H), 3.78 (s, 3H), 7.45 (s, 1H), 7.53 (dd, 1H, J = 8.7 Hz, J = 1.8 Hz), 7.68 (d, 1H, J = 8.7 Hz), 8.01 (s, 1H), 9.99 (s, 1H, OH); ^{13}C NMR (DMSO-d_6) δ 30.86, 34.60, 60.72, 116.47, 117.73, 124.30, 124.91, 125.81, 126.40, 128.75, 138.42, 145.52, 147.42; MS *m/z* (relative intensity) 266 (M^+, 22), 264 (M^+, 70), 249, (100). Anal. Calcd for $C_{15}H_{17}ClO_2$: C, 68.01; H, 6.47; Cl, 13.39. Found: C, 67.95; H, 6.40; Cl, 13.29.

3-Chloro-2,7-dimethoxy-1-naphthol (18d): white crystals; mp 106−107 °C (*n*-hexane); yield 1.79 g (75%); IR 3440−3380 (vs, br), 1590 (s) (OH, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.79 (s, 3H), 3.86 (s, 3H), 7.10 (dd, 1H, J = 8.9 Hz, J = 2.5 Hz), 7.39 (s, 1H), 7.46 (s, 1H), 7.68 (d, 1H, J = 9.0 Hz), 9.93 (s, 1H, OH); ^{13}C NMR (DMSO-d_6) δ 55.05, 60.70, 100.31, 118.13, 118.59, 123.74, 125.69, 125.88, 128.36, 138.87, 144.60, 156.89; MS *m/z* (relative intensity) 240 (M^+, 33), 238 (M^+, 100), 223 (75), 195 (22). Anal. Calcd for $C_{12}H_{11}ClO_3$: C, 60.39; H, 4.65; Cl, 14.85. Found: C, 60.41; H, 4.61; Cl, 14.57.

3-Chloro-7-iodo-2-methoxy-1-naphthol (18e): white crystals; mp 123−125 °C (*n*-hexane); yield 2.71 g (81%); IR 3380−3320 (s, br), 1570 (m) (OH, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.79 (s, 3H), 7.53 (s, 1H), 7.56 (d, 1H, J = 8.6 Hz), 7.69 (d, 1H, J = 8.6 Hz), 8.44 (s, 1H), 10.27 (s, 1H, OH); ^{13}C NMR (DMSO-d_6) δ 60.84, 91.17, 118.44, 126.20, 127.55, 128.60, 129.07, 130.36, 134.21, 139.11, 144.60; MS *m/z* (relative intensity) 336 (M^+, 32), 334 (M^+, 100), 319 (58), 291 (14). Anal. Calcd for $C_{11}H_8ClIO_2$: C, 39.49; H, 2.41; Cl, 10.60; *J*, 37.93. Found: C, 39.91; H, 2.50; Cl, 10.85; I, 37.32.

3,5,8-Trichloro-2-methoxy-1-naphthol (18f): white crystals; mp 139−140 °C (toluene); yield 1.97 g (71%); IR 3430 (s), 1575 (m) (OH, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.80 (d, 3H, J = 2.3 Hz), 7.43 (dd, 1H, J = 8.1 Hz, J = 2.2 Hz), 7.53 (dd, 1H, J = 8.1 Hz, J = 2.1 Hz), 7.68 (d, 1H, J = 2.2 Hz), 10.33 (s, 1H, OH); ^{13}C NMR (DMSO-d_6) δ 60.86, 114.72, 121.87, 126.45, 128.05, 128.28, 128.52, 129.10, 140.95, 147.75; MS *m/z* (relative intensity) 282, (M^+, 4), 280 (M^+, 31), 278 (M^+, 97), 276 (M^+, 100), 261 (99), 233 (42). Anal. Calcd for $C_{11}H_7Cl_3O_2$: C, 47.61; H, 2.54; Cl, 38.32. Found: C, 48.00; H, 2.47; Cl, 37.77.

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