3 can be obtained in two or three steps from commercial materials, the approach looks valuable for synthesis.

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Supplementary Material Available: Spectroscopic information for compounds **4**, **6**, and **7a** (1 page). Ordering information is given on any current masthead page.

Rearrangement of 4-Chloro-4-aryl(or alkenyl)cyclobutenones to *p*-Chlorophenols

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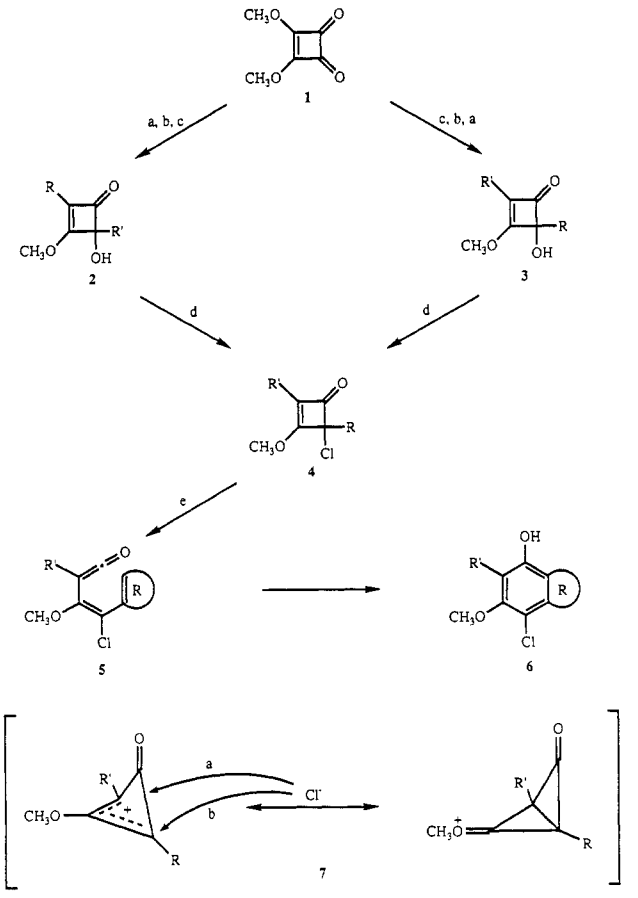
Summary: The synthesis and thermolysis of 4-chloro-4-aryl(or alkenyl)cyclobutenones is described. This results in a general and synthetically useful route to highly substituted chlorophenols and chloronaphthols. The chlorocyclobutenones were prepared from the related 4-hydroxy derivatives upon treatment with thionyl chloride in the presence of pyridine. The chlorination is regiospecific and predictable based upon a proposed mechanistic paradigm.

Sir: Previously, ring expansions of 4-alkynyl-4-hydroxy- and 4-aryl-4-hydroxycyclobutenones to respectively 1,4-benzoquinones and annelated hydroquinones were reported.[1,2] An extension of these rearrangements is now presented which shows that the thermolysis of 4-chloro-4-aryl(or alkenyl)cyclobutenones provides an efficient regiospecific route to substituted chlorophenols and chloronaphthols. The regiospecificity associated with this methodology is of particular interest and evolves from the overall transformation outlined in Scheme I. That is, starting with dimethylsquarate, **1**, the regioisomeric cyclobutenones **2** and **3** can be independently prepared.[3,4] *Interestingly, both of these cyclobutenones give the same 4-chloro derivative 4 upon treatment with thionyl chloride in methylene chloride and in the presence of pyridine, and the position of chlorination is predictable and dependent upon the substituents R and R'.* Thermolysis of **4** in refluxing *p*-xylene results in selective electrocyclic ring opening to the intermediate conjugated ketene **5**, which leads to the chlorophenols (or naphthols) **6** upon electrocyclic ring closure.

The selectivity of the chlorination of **2** and/or **3** is of particular note and deserves further comment. The results show that the substituents at positions 2 and 4 of the cyclobutenones **2** and **3** significantly influence the regiochemistry of the chlorination. Specifically, since the respective pairs of cyclobutenones give the same 4-chloro derivative, a common intermediate is obvious, and this is assumed to be the cationic species represented by structure **7**, a homoaromatic carbocation which should gain additional stabilization by electron donation of the methoxy substituent.[5,6]

Scheme I[a]



[a] Reagents: (a) RLi, THF, −78 °C; (b) TFAA/H^+; (c) R'Li, THF, −78 °C; (d) $SOCl_2$/pyridine, CH_2Cl_2, 0 °C; (e) *p*-xylene, 138 °C.

A very useful prediction of the site of chlorination evolves by further consideration of this paradigm. *That*

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Table I. Physical Properties of Final Products[a]

compd	mp, °C	NMR ($CDCl_3$), δ	IR, cm^{-1}	MS (rel int)
9	oil	^1H 3.47 (s, 3 H), 4.99 (s, 1 H), 6.75 (d, J = 8.8 Hz, 1 H), 7.27 (d, J = 8.8 Hz, 1 H), 7.38–7.52 (m, 5 H); ^{13}C 60.61, 112.12, 119.24, 123.80, 128.58, 129.27, 129.69, 130.27, 131.66, 152.42, 153.70	3456, 3030, 2940, 1610, 1580, 1465, 1440, 1410, 1330, 1290, 1220, 1170, 1060, 1040, 950, 810, 760, 710, 660	234 (100, EI)
11	oil	^1H 0.97 (t, J = 7.2 Hz, 3 H), 1.45–1.70 (m, 4 H), 2.55 (t, J = 7.2 Hz, 2 H), 3.95 (s, 3 H), 5.81 (s, 1 H), 6.66 (d, J = 8.7 Hz, 1 H), 7.18 (d, J = 9.0 Hz, 1 H); ^{13}C 13.49, 19.43, 21.94, 30.54, 60.80, 70.50, 102.88, 106.50, 110.61, 118.36, 129.83, 156.28, 156.41	3480, 2940, 2870, 2220, 1570, 1465, 1415, 1340, 1300, 1220, 1180, 1055, 810, 710	238 (47, EI)
14	49–50	^1H 0.94 (t, J = 7.2 Hz, 3 H), 1.37–1.59 (m, 4 H), 2.29 (s, 3 H), 2.61 (t, J = 7.5 Hz, 2 H), 3.82 (s, 3 H), 4.61 (s, 1 H), 6.48 (s, 1 H); ^{13}C 13.92, 20.01, 22.30, 24.11, 31.93, 60.32, 113.25, 119.81, 121.71, 134.93, 152.51, 154.75	3420, 2960, 2940, 2870, 1610, 1580, 1460, 1330, 1210, 1170, 1110, 1060, 1010, 950, 915, 845, 650, 610	228 (25, EI)
16	oil	^1H 0.96 (t, J = 7.2 Hz, 3 H), 1.45 (m, 2 H), 1.60 (m, 2 H), 2.79 (t, J = 7.5 Hz, 2 H), 3.94 (s, 3 H), 7.46 (t, J = 7.5 Hz, 1 H), 7.55 (t, J = 7.5 Hz, 1 H), 8.10 (d, J = 8.1 Hz, 1 H), 8.19 (d, J = 8.4 Hz, 1 H)	3500, 2960, 2940, 2860, 1630, 1590, 1570, 1500, 1450, 1390, 1345, 1260, 1210, 1120, 1060, 990, 930, 760	264 (100, EI)
17	oil	^1H 0.96 (t, J = 7.4 Hz, 3 H), 1.47 (sextet, J = 7.4 Hz, 2 H), 2.50 (q, J = 7.4 Hz, 2 H), 4.35 (s, 3 H), 5.46 (t, J = 7.9 Hz, 1 H), 7.21–7.37 (m, 3 H), 7.73 (d, J = 7.4 Hz, 2 H); ^{13}C 13.56, 23.18, 29.94, 59.92, 118.02, 126.13, 127.71, 128.40, 129.48, 133.37, 144.99, 181.74, 185.68	3050, 2960, 2920, 2860, 1755, 1680, 1585, 1490, 1450, 1370, 1310, 1060, 1010, 790, 750, 690	228 (57, EI)
19	52–53	^1H 0.98 (t, J = 7.2 Hz, 3 H), 1.50–1.58 (m, 2 H), 1.64–1.71 (m, 2 H), 2.60 (t, J = 7.1 Hz, 2 H), 4.01 (s, 3 H), 6.39 (s, 1 H), 7.44–7.49 (m, 1 H), 7.56–7.62 (m, 1 H), 8.15–8.20 (m, 2 H)	3500, 3020, 2970, 2940, 2870, 2220, 1630, 1600, 1580, 1500, 1465, 1430, 1395, 1300, 1210, 1130, 1100, 1020, 990, 920, 670, 645	288 (72, EI)
22	oil	^1H 1.37 (d, J = 6.3 Hz, 6 H), 3.69 (s, 3 H), 4.61 (septet, J = 6.3 Hz, 1 H), 5.35 (s, 1 H), 7.40–7.60 (m, 7 H), 8.14 (d, J = 8.7 Hz, 1 H), 8.17 (d, J = 9.3 Hz, 1 H); ^{13}C 22.82, 60.49, 75.68, 118.24, 121.46, 122.10, 122.25, 124.43, 126.36, 128.24, 129.31, 130.30, 130.66, 132.87, 138.46, 144.56, 146.93	3550, 2980, 2940, 1630, 1600, 1500, 1460, 1420, 1385, 1300, 1285, 1215, 1110, 1070, 1050, 1020, 950, 770, 760	308 (32, EI)
24	waxy solid	^1H 3.43 (s, 3 H), 5.86 (s, 1 H), 7.03–7.06 (m, 3 H), 7.13–7.18 (m, 2 H), 7.46–7.60 (m, 7 H), 8.43 (d, J = 8.3 Hz, 1 H), 8.47 (d, J = 8.7 Hz, 1 H); ^{13}C 61.54, 111.32, 118.41, 122.54, 122.90, 124.64, 124.90, 125.89, 125.94, 128.24, 128.58, 128.72, 129.50, 130.72, 132.31, 135.83, 139.17, 151,45, 159.66	3540, 3070, 3010, 2940, 1620, 1585, 1560, 1495, 1480, 1415, 1380, 1295, 1275, 1095, 910, 700	358 (100, EI)

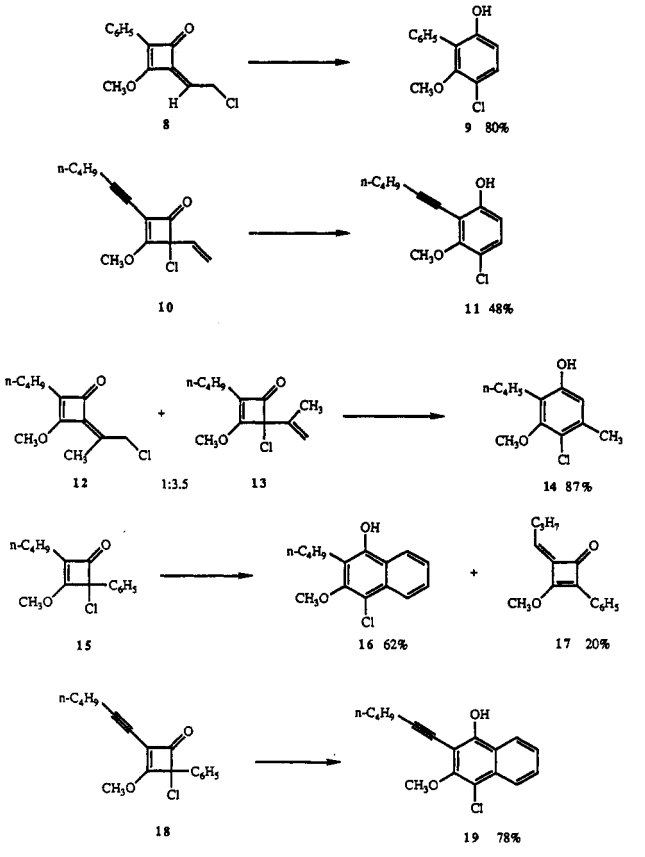
[a] Analytical data are all in agreement with the presented structures.

is, chlorination takes place preferentially at the position gaining the more cation stabilization; this follows the general order of allyl > benzyl > alkyl > propargyl.[7] Thus, the cyclobutenones **8**, **10**, **12**, **13**, **15**, and **18** (Scheme II) were obtained as the chloro derivative from the respective 4-hydroxycyclobutenones corresponding to **2** and/or **3**.

Some specific details for these transformations follow. The cyclobutenones **10**, **12**, and **13** were obtained from the respective 2-alkenyl-4-hydroxycyclobutenones, i.e., from those compounds having the hydroxy group of the precursors attached to a different C atom than the chloro group in the resulting products. Thus, chlorination at the allylic position is most favorable as predicted from the noted paradigm. It is of interest that terminal allylic chlorination to give the methylenecyclobutenone **8** results from both 2-ethenyl-4-hydroxy-3-methoxy-4-phenylcyclobutenone and the regioisomeric 4-ethenyl-4-hydroxy-3-methoxy-2-phenylcyclobutenone and that internal allylic chlorination to **10** arises from the 4-hexynyl analog; this selectivity is not yet understood. Furthermore, it is of particular interest that **8** ring expands to **9** in reasonable yield, a transformation which must involve an equilibrium between **8** and its 4-chlorocyclobutenone regioisomer.

As noted above for **8**, the synthesis of **15** and **18** was accomplished from both regioisomeric pairs of 4-hydroxycyclobutenones corresponding, in general, to **2** and **3** (Scheme I). Again, the fact that both respective pairs lead to exclusively **15** or **18** is consistent with the mechanistic model outlined above. Furthermore, the formation of **15** shows that benzylic chlorination is more favorable than attack at the alkyl site and **18** reflects the preference of reaction at the benzylic over the propargylic site.

Scheme II



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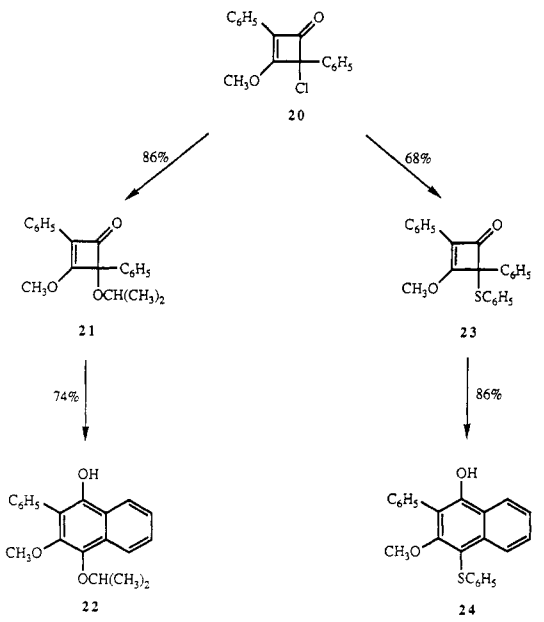
Scheme III



The specific examples of the rearrangement given in Scheme II illustrate useful synthetic routes to highly substituted chlorophenols and chloronaphthols. Generation of **9**, **11**, **14**, and **19** proceeds without complications. However, thermolysis of **15** gives the expected chloronapthol **16** as the major product, and the methylenecyclobutenone **17** is also realized as a minor product. This is an interesting result when compared with the fact that the structurally analogous cyclobutenone **13** gives only the phenol **14** upon thermolysis. Thus, it is assumed that **15** undergoes an intramolecular elimination of HCl to give **17** in competition with electrocyclic ring open to the conjugated ketene, the intermediate presumed to be formed in the rate-determining step on the pathway to the naphthol **16**. On the other hand, electrocyclic ring opening of **13** is more favorable than that of **15** and, as a result, the elimination pathway is circumvented. That **13** rearranges at a faster rate than **15** is not unreasonable based upon qualitative observations of related systems. For example, we have observed that 4-hydroxy-4-alkenylcyclobutenones ring expand faster than their 4-aryl counterparts.

Finally, it is reported that the chlorocyclobutenones may function as precursors to a large variety of other substituted phenols since the chloro substituent is labile to nucleophilic displacement (Scheme III). For example, the cyclobutenone **20** is readily converted to **21** or **23** upon respectively treatment with isopropyl alcohol or thiophenol. These derivatives then give the phenols **22** or **24** in good yields upon thermolysis in refluxing *p*-xylene.

The structures of all of the products are based upon their characteristic spectral properties (Table I). In addition, the methylenecyclobutenones, **8** and **17**, were shown to have the indicated *Z* stereochemistry by DNOE studies.

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Unsolvated Magnesium Diisopropylamide in Organic Synthesis. 2. Reduction of Nitro, Nitroso, and Azoxy Compounds

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Summary: The reduction of nitro, nitroso, and azoxy compounds has been effected by using unsolvated magnesium diisopropylamide (MDA). The resultant products have been found to depend on the structure of the substrate and the ratio of substrate to MDA used.

Sir: Our recent finding that unsolvated magnesium diisopropylamide (MDA) easily reduces aldehydes and ketones[1] has prompted us to study this novel reagent's ability to reduce other synthetically important functional groups. Because of the importance of the reduction of nitro, nitroso, and azoxy functional groups in organic chemistry,[2,3] and since we desired a novel method for the preparation of unsymmetrical azo compounds for photochemical study, we undertook an investigation of the reduction of these types of substrates with unsolvated MDA.[4] We have found that MDA will readily reduce all of these groups in alkanes media (Table I).

Since many variations of the reductions presented here remain to be studied, the scope of these reductions is potentially very broad. However, even at this early stage of the investigation several trends are becoming apparent: (1) the reduction of nitro-substituted benzenes can be stopped at the azoxy or azo or taken to the amine stage by adjusting the amount of MDA used (Table I entries 3 vs 10 and 4 vs 9); (2) the reduction of nitro aromatic–carbocyclic compounds, other than benzene, seems to yield only the amine under the same reaction conditions (Table I, entries 5 and 6); (3) unlike the reduction of aromatic nitro compounds, the reduction of aliphatic nitro com-

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