

A Tandem Silica-induced Ring-opening and Cyclisation of 1-Aryl-1-chlorocyclopropanes leading to Indenes

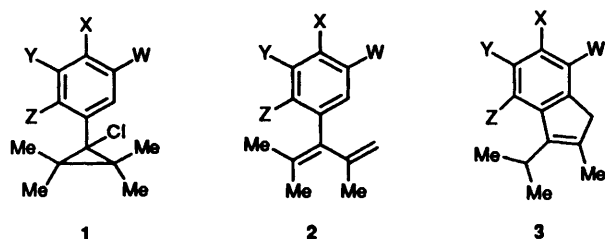
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Reaction of a number of methoxy-substituted 1-aryl-1-chloro-2-methylcyclopropanes with silica and carbon tetrachloride at 20 °C leads to indenenes, in a process which may involve ring-opening to a diene with loss of HCl, followed by acid-induced cyclisation.

We have previously reported that the reaction of 1-chloro-1-thienylcyclopropanes with silica in carbon tetrachloride can lead to ring-opening of the cyclopropane with loss of hydrogen chloride and the formation of a diene.¹ We now report that similar treatment of a number of 1-aryl-1-chlorocyclopropanes having electron-releasing groups in the aromatic ring leads instead to eventual substitution into the aryl group with the formation of an indene.

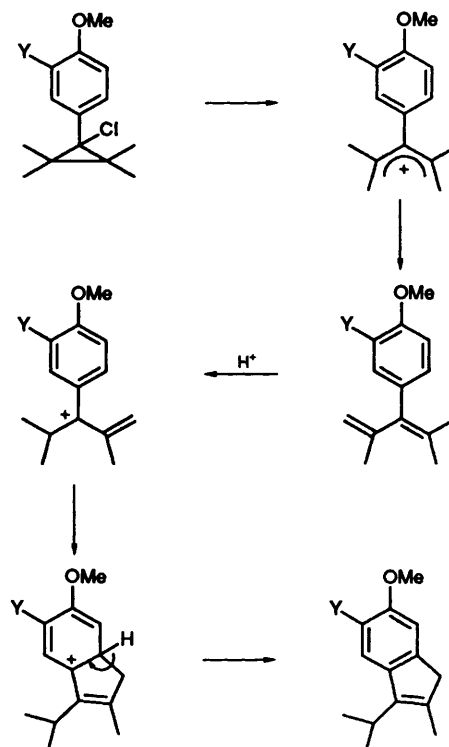
Treatment of the cyclopropane **1g**† with silica‡ and carbon tetrachloride for 18 h at 20 °C led to the diene **2g**§ in a reaction apparently parallel to that of 1-chloro-1-thienylcyclopropanes.¹ Under the same conditions, the cyclopropane **1a** was converted into the indene **3a**, which showed a characteristic pattern for a 1,2,4-trisubstituted benzene ring in the ¹H NMR spectrum, as well as a methine hydrogen as a septet (*J* 7.1 Hz) at δ 3.08, a methylene group at 3.21 and the expected signals for the methyl groups.



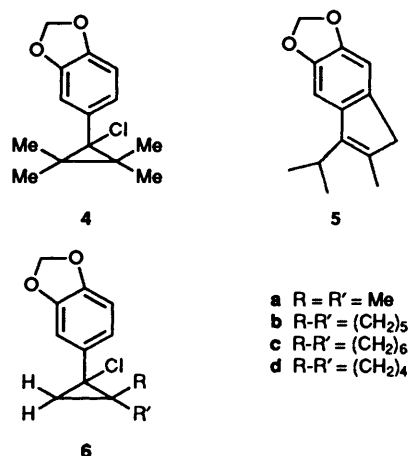
- | | |
|--------------------------|--------------------------|
| a X = OMe, W = Y = Z = H | e W = Z = OMe, X = Y = H |
| b X = Y = OMe, W = Z = H | f Y = Z = OMe, X = W = H |
| c X = Z = OMe, W = Y = H | g W = Y = OMe, X = Z = H |
| d W = X = Y = OMe, Z = H | |

In the same way **1b** and **4** were each converted into a single indene **3b** or **5** respectively; the ¹H NMR spectra of these included signals for just two aromatic hydrogens, as one singlet in the case of **2b** and two singlets in the case of **5**. The formation of indenenes may be rationalised in terms of an initial cyclopropyl-allyl ring-opening, promoted by the strongly electron-releasing substituent.⁶ Deprotonation would then generate the corresponding diene **2** together with a molecule of HCl; readdition of the proton, directed again by the electron-releasing 4-substituent, followed by cyclisation would lead to the indene (Scheme 1).||

In support of this, treatment of a mixture of the diene **10** and



Scheme 1



- | |
|--|
| a R = R' = Me |
| b R-R' = (CH ₂) ₅ |
| c R-R' = (CH ₂) ₆ |
| d R-R' = (CH ₂) ₄ |

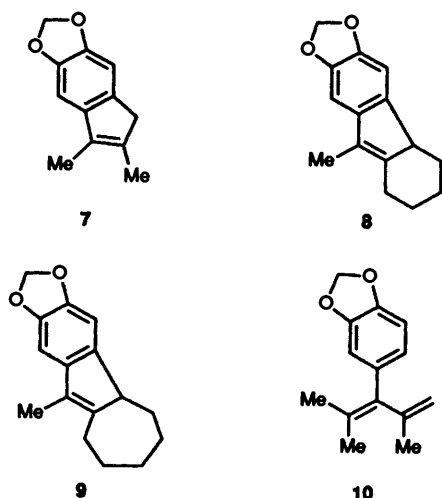
† The 1-aryl-1-chlorocyclopropanes were prepared by reaction of the corresponding dichloromethyl-benzene with potassium *t*-butoxide in the presence of an alkene in dimethoxyethane solution.

‡ Purchased from BDH; 40–63 μm or 130–250 μm.

§ For a recent alternative route to 2-arylbuta-1,3-dienes see J. E. Baldwin, P. A. R. Bennett and A. K. Forrest, *J. Chem. Soc., Chem. Commun.*, 1987, 250.

¶ Compound **1** (W = X = Y = Z = H) was recovered unchanged after treatment with SiO₂-CCl₄ for 18 h as above.

|| Reaction of the diene **10** with toluene-*p*-sulfonic acid in benzene or carbon tetrachloride for 24 h at reflux led cleanly to the indene **5**. No reaction occurred over a period of 24 h at 20 °C, or if the purified diene was stirred with SiO₂-CCl₄ for 18 h at 20 °C.



silica in carbon tetrachloride with hydrogen chloride for 1 min at 20 °C gave the indene **5** (94%), whereas the diene was unchanged after 18 h if the silica was omitted.

The reaction was also successful with less substituted cyclopropanes; thus **6a** was converted into **7**, while the tricyclic derivatives **6b** and **6c** underwent an efficient conversion into fused tricyclic systems **8** and **9**. In the case of the cyclopentane derivative **6d**, the reaction led to a complex mixture of products.

An indene was also formed from the 2,4-dimethoxyphenyl-cyclopropane **1c**, but the isomeric dimethoxy-compounds **1f** and **1g** and the trimethoxy-derivative **1d** are instead converted into dienes **2d**, **2f** and **2g** respectively, while the dimethoxy compound **1e** was unreactive to silica under the conditions employed.

The details of the actual effect of the silica* on these reactions and of the substituent effects are the subject of further study.

* The use of silica as a reagent has recently been reviewed (K. Smith, *Bull. Soc. Chim. France*, 1989, 272).

Table 1 Ring-opening of 1-aryl-1-chlorocyclopropanes over silica

Cyclopropane	Diene	Products	
		(%)	Indene (%)
1a	—	—	3a 72
1b	—	—	3b 100
1c	—	—	3c 67
1d	2d	33	—
1e	—	—	—
1f	2f	36	—
1g	2g	90	—
4	—	—	8 75 ^a
6a	—	—	7 63
6b	—	—	8 65
6c	—	—	9 70

^a The reaction of **4** with SiO₂-CCl₄ was very dependent on the purity of the starting material. When **4** was used direct from the reaction of 1-dichloromethyl-3,4-methylenedioxybenzene with potassium *t*-butoxide and 2,3-dimethylbut-2-ene in dimethoxyethane without recrystallisation, reaction with SiO₂-CCl₄ for 18 h at 20 °C led to the diene **10** (75%).

Nonetheless the ready availability of cyclopropanes such as **1** and the mild reaction conditions suggest that this might provide a ready access to cyclopentenenes fused to a range of ring systems.

Acknowledgements

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References

- M. S. Baird and I. Bruce, UK Pa 89 25977.4; *J. Chem. Res.*, 1989, (S), 376, (M), 2872; 1990, (S), 134, (M), 0946.

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