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Thermal Rearrangement of Halogenated Dimethylenecyclobutane and Methylenecyclobutene Derivatives

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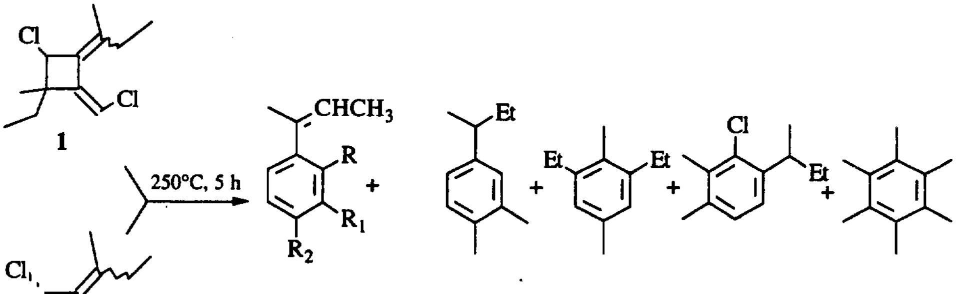
Abstract : Upon heating, dichlorodimethylenecyclobutanes (**1**, **2**, **18**) undergo rearrangements that yield benzene derivatives including styrene adducts. Preparation of postulated intermediates (**10**, **23**) and study of their pyrolytic behaviour allow to unambiguously establish the mechanism of formation of the styrene derivatives. Copyright © 1996 Published by Elsevier Science Ltd

Thermally induced rearrangements of cyclobutane derivatives can occur with ring retention[1] or expansion as in the case of vinylcyclobutanes or alkylidenecyclobutanes.[2,3] Aromatization can also take place[3] and, in some cases, a mechanism involving a ketene/cyclobutene equilibrium has been proposed.[3f-h] Some years ago, we described the conversion, by pyrolysis, of two dihalogenated dimethylenecyclobutanes into aromatic hydrocarbons and briefly envisaged a mechanistic pathway for this rearrangement.[3a] Continuing our studies in this field, we now report on the thermal rearrangement of two other dihalogenated dimethylenecyclobutanes (**1** and **2**) whose unsymmetric olefin substitution pattern allows the unambiguous confirmation and generalization of the mechanism of formation of the styrene adducts formed consecutively to the heating of the title compounds.

Pyrolysis[4] of **1** and its isomer **2**, both easily prepared by dimerization of 1-chloro-3-methyl-1,2-pentadiene,[5] afforded, in 85 and 60% total yield respectively, the same rearranged adducts **3-9**[6] (Scheme 1). We have previously suggested that the formation of these aromatic compounds could be explained by either an equilibrium between **1** and **2** at high temperature or the formation, from both isomers, of common intermediates leading to identical rearranged adducts.[3a] To confirm this latter hypothesis, we particularly studied the formation of the styrene derivatives (**3-5**). As several derivatives could be proposed, from **1** or **2**, as precursor of the hypothetical intermediates leading to the styrene adducts, we preliminary studied the pyrolysis of **10**, a compound prepared from **1**.[5] Delightfully, heating of **10** (250°C, 1h) afforded exclusively styrenes **3**, **4**, and **5** in 8, 86, and 6% yield respectively.

Scheme 1



3: $R=R_1=CH_3$; $R_2=H$ **6** **7** **8** **9**

4: $R=R_2=H$; $R_2=C_2H_5$

5: $R=H$; $R_1=R_2=CH_3$

Yields (%) From 1: 3 (6); 4 (40); 5 (3); 6 (32); 7 12); 8 (1); 9 (6)

From 2: 3 (14); 4 (14); 5 (15); 6 (12); 7 (4); 8 (32); 9 (8)

At this stage, it became reasonable to propose, as one of the possibly multiple primary rearrangement steps, the thermal elimination of an hydrochloric acid molecule from **1** and **2** (Scheme 2); this leading to divinylallenes **12** and **13** respectively, *via* the chloromethylenecyclobutenes **10** and **11** whose thermally induced opening is well established.[7] From **12** and **13**, three different pathways could be envisaged, both affording the same intermediates **14**, **15** and **17** (Scheme 2).

From **12** a) a 1-5 sigmatropic shift of an hydrogen atom from a methyl group may lead to intermediate **15** (path A, Scheme 2),

b) a 1-5 sigmatropic rearrangement of an hydrogen atom belonging to a methylene group may lead to **14** (path B),

c) a 1-3 sigmatropic shift of a methyl group arising from the ethyl substituent may afford intermediate **17** *via* **16** and either two 1-2 hydrogen shifts[8] or more likely an additional prototropic rearrangement (path C).

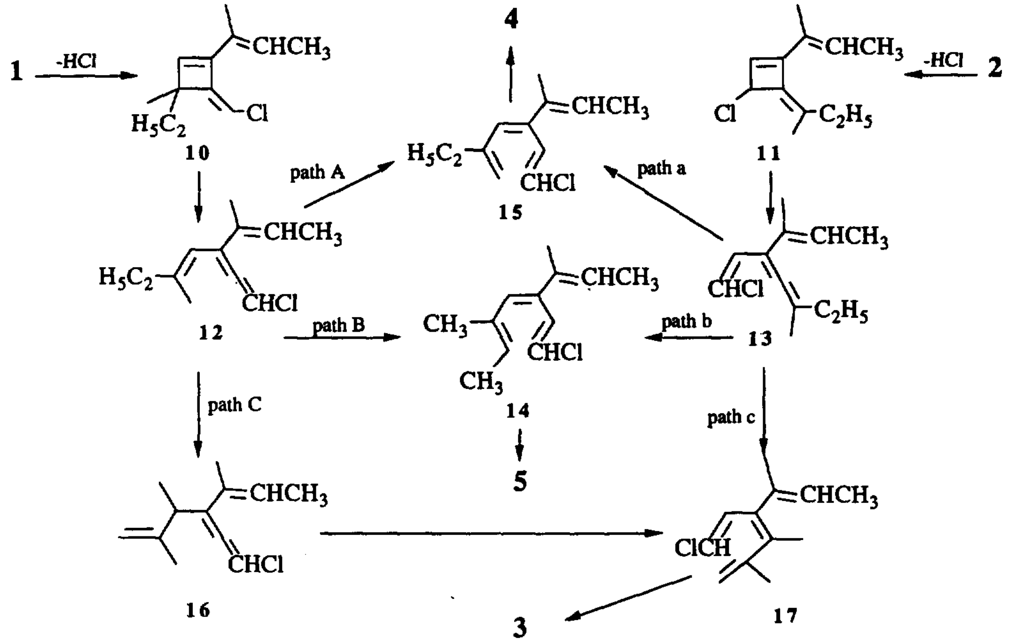
From **13** a) a 1-3 sigmatropic shift of an hydrogen atom from a methyl group may lead to intermediate **15** (path a),

b) a 1-3 sigmatropic rearrangement of an hydrogen atom from a methylene group may lead to **14** (path b),

c) a 1-3 sigmatropic shift of a methyl group arising from the ethyl substituent may afford intermediate **17** (path c); thermal cyclization of **14**, **15** and **17** followed by aromatization with elimination of an HCl molecule finally yielding **4**, **5** and **3** respectively.

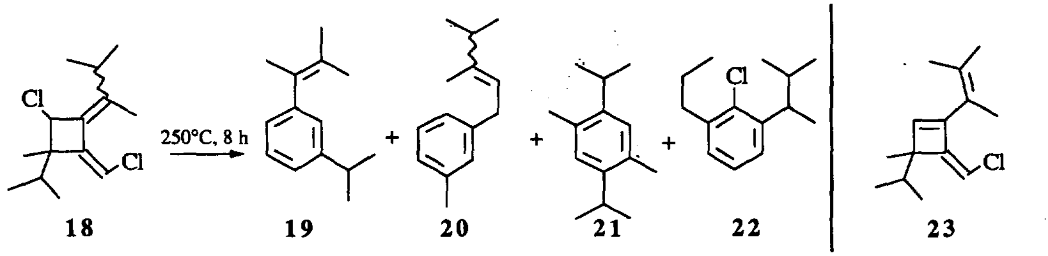
To further confirm our proposed mechanism, we also studied the thermal rearrangement of **18**, another dihalogenated dimethylenecyclobutane prepared by dimerization of 1-chloro-3,4-dimethyl-1,2-pentadiene.[5]

Scheme 2



Pyrolysis of **18** required a slightly longer heating time and afforded in 60% yield a complexe mixture of compounds. Amongst the four major one, depicted scheme 3, styrene **19** was of particular interest. To demonstrate the involvement of a chloromethylenecyclobutene derivative in its formation, we investigated the pyrolytic behaviour of **23** already prepared in our laboratory.[5] As expected, pyrolysis of **23** afforded **19** as main product (72% yield).

Scheme 3



Yields (%) : 19(22); 20(13); 21(23); 22(17)

In summary, this study provides, in addition to our previous study,[3a] a general demonstration for the mechanism of formation of the styrene derivatives elaborated by pyrolysis of dichlorodimethylenecyclobutanes.

The key intermediates are allylchloromethylenecyclobutenes that undergo various rearrangements before yielding styrene compounds. Attempts to use these rearrangements for the synthesis of biologically active compounds will be reported in a forthcoming article.

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4. For the pyrolysis experiments, 1 mL of material was introduced in a tube that was then sealed under reduced pressure (10^{-2} mm Hg) and then heated.

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