

Anodic Oxidation of 1-Aryl-2,2-dihalogenocyclopropanes in Methanol or Acetonitrile Media

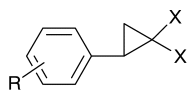
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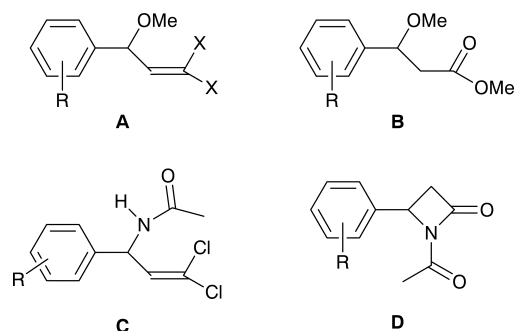
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3-Aryl-1,1-dichloro-3-methoxypropenes, methyl 3-aryl-3-methoxypropionates and 3-acetamido-3-aryl-1,1-dichloro-propenes are obtained along with *N*-acetyl-4-aryllactams *via* anodic oxidation of 1-aryl-2,2-dichlorocyclopropanes in methanol and acetonitrile solutions, respectively.

The electrolysis of cyclopropanes has been reported.⁶⁻⁹ 1,1-Dichloro-3-phenylpropene, methyl 3-methoxy-3-phenylpropionates and methyl cinnamate have been reported as products of the electrolysis of 2,2-dichloro-3-phenylcyclopropanecarboxylic acids⁶ and 2,2-dichloro-1-phenylcyclopropane⁷ in methanol. In our continuing studies of 1-aryl-2,2-dihalogenocyclopropanes,⁵ a series of 1-aryl-2,2-dichlorocyclopropanes and 2,2-dibromo-1-phenylcyclopropane was oxidized at a constant applied voltage in either methanol or acetonitrile solution containing a suitable electrolyte. During anodic oxidation, the solvent serves as a nucleophilic reagent and participates in the reaction. By means of these processes, dihalogenocyclopropanes can be utilized to prepare the series of new compounds.



- | | |
|--------------------|---------------------|
| 1 X = Br, R = H | 7 X = Cl, R = 4-Br |
| 2 X = Cl, R = H | 8 X = Cl, R = 3-Br |
| 3 X = Cl, R = 4-F | 9 X = Cl, R = 4-Me |
| 4 X = Cl, R = 3-F | 10 X = Cl, R = 3-Me |
| 5 X = Cl, R = 4-Cl | 11 X = Cl, R = 2-Me |
| 6 X = Cl, R = 3-Cl | |



To carry out the electrochemical oxidations under optimized conditions, we arbitrarily chose **2** as a model compound and studied its oxidation in methanol under various conditions. The recovery of the starting material was examined in each case. Table 1 summarizes the effects of the supporting electrolyte, added base and the terminal voltage used for the electrolysis of 2,2-dichloro-1-phenylcyclopropane. Examination of these results shown in Table 1 led us to conclude that the use of perchlorate as the electrolyte and a 24 h reaction period were suitable conditions for the present study (entries 1, 2, 9). Among the electrolytes tested, the quaternary ammonium salts gave poor electro-oxidation results, because halide ions are more easily oxidized than the cyclopropane derivatives (entries 15-18).

Table 1 Recovery of compound **2** from the reactions under various conditions^a

| Entry | Potential/V | Conditions | | Recovery (%) |
|-------|-------------|---|------------------------|--------------|
| | | Electrolyte | Base/solvent | |
| 1 | 5.0 | NaClO ₄ | MeOH | 0.0 |
| 2 | 4.0 | NaClO ₄ | MeOH | 0.0 |
| 3 | 3.0 | NaClO ₄ | MeOH | 99.5 |
| 4 | 4.0 | NaClO ₄ | MeCN | 0.0 |
| 5 | 3.0 | NaClO ₄ | MeCN | 98.5 |
| 6 | 4.0 | NaClO ₄ | pyridine/MeOH | 14.7 |
| 7 | 4.0 | NaClO ₄ | pyridine/MeCN | 12.3 |
| 8 | 4.0 | NaClO ₄ | ^b MeOH | 44.3 |
| 9 | 4.0 | NaClO ₄ | ^b MeOH | 50.0 |
| 10 | 4.0 | NaClO ₄ | ^c MeOH | 84.8 |
| 11 | 4.0 | NaClO ₄ | Et ₃ N/MeOH | 95.7 |
| 12 | 4.0 | NaClO ₄ | H ₂ O/MeOH | 33.2 |
| 13 | 4.0 | LiClO ₄ | MeOH | 0.0 |
| 14 | 4.0 | LiClO ₄ | MeCN | 0.0 |
| 15 | 4.0 | Et ₄ N ⁺ Cl ⁻ | MeOH | 83.0 |
| 16 | 4.0 | Et ₄ N ⁺ Br ⁻ | MeOH | 92.0 |
| 17 | 4.0 | Et ₄ N ⁺ I ⁻ | MeOH | 95.0 |
| 18 | 4.0 | Et ₄ N ⁺ BF ₄ ⁻ | MeOH | 75.7 |

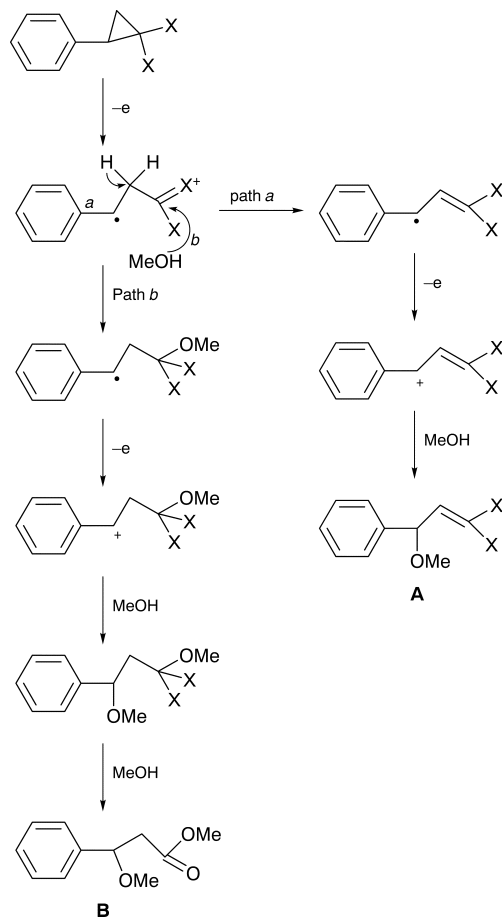
^aPotential: terminal voltage; concentration of electrolyte was 0.5 mol dm⁻³ in methanol (MeOH) or acetonitrile MeCN solution; the ratio of methanol: base was 10:1 vol %; the recovery yields were estimated by using GLC from the area ratio. ^b3,5-Dimethylpyridine. ^c2,4,6-Trimethylpyridine.

According to previous reports, cleavage of the carbon-chlorine bond might result in hydrogen chloride as a side product.¹¹ Some bases were added to the solution in order to remove acid and to enhance the forward process. Unexpectedly, the bases decreased the oxidation efficiency, perhaps due to competition between the base and the cyclopropane derivatives in the oxidation process. This result was clearly shown with the use of a bulky base (entries 8, 9) and of a stronger base (triethylamine, entry 11). Water also reduced the reactivity of compound **2** in the oxidation process (entry 12).

In methanol solution, the resultant products from the electrolysis process were worked up after the mixture was poured into water, extracted with diethyl ether, and then separated by chromatography using thin-layer chromatography (TLC) or gas-liquid chromatography (GLC). Two major products were identified as 3-methoxy-3-phenyl-1,1-dihalogenopropene (**A**) and methyl 3-methoxy-3-phenylpropionate (**B**). Two minor compounds, benzoic acids and their methyl esters, were also identified by GC/MS analysis.

Compound **2B** was first believed to be formed through compound **2A**. Pure **2A** was electrolysed under the same conditions as above for a period of 24 h. However, no change was observed *vs.* compound **2A** by GLC analysis. When the electrolysis of compound **2** was also monitored during the time course, we found that both **2A** and **2B**

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Scheme 1

were observed initially. In this study, the halogen atoms are oxidized by the loss of an electron from a lone-pair; cleavage of the carbon-carbon bond of the cyclopropane ring then follows to result in a benzylic radical. Compound A is presumably formed by the loss of a proton followed by oxidation to a cationic intermediate which undergoes methanolysis as shown in the proposed Scheme 1.^{13,14} On the other hand, methanolysis is followed by oxidation to yield a benzylic cation for the second methanolysis. This *gem*-dichloro intermediate can undergo solvolysis as in the alcoholysis of the trihalogenomethyl groups.^{15,16}

The same procedure was applied using acetonitrile instead of methanol with sodium perchlorate as the supporting electrolyte. After work-up, 3-acetamido-3-aryl-1,1-dichloro-

propene (C) and *N*-acetyl-4-aryllactam (D) were isolated in good yields by means of column chromatography.

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Techniques used: IR, GLC, ¹H NMR, ¹³C NMR, MS

References: 20

Scheme: 1

Table 2: Physical and analytical data for compounds 3-methoxy-3-phenyl-1,1-dihalogenopropene (A) and methyl 3-methoxy-3-phenylpropionate (B)

Table 3: Spectral data of 3-methoxy-3-phenyl-1,1-dihalogenopropene (A) and methyl 3-methoxy-3-phenylpropionate (B)

Table 4: Physical properties of 3-acetamido-3-aryl-1,1-dichloropropane (C) and *N*-acetyl-4-aryllactam (D)

Table 5: Spectral data of 3-acetamido-3-aryl-1,1-dichloropropane (C) and *N*-acetyl-4-aryllactam (D)

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