1,*n*-Radical Ions. The Electrochemical Oxidation of 1,1,2,2-Tetraphenylcyclopropane

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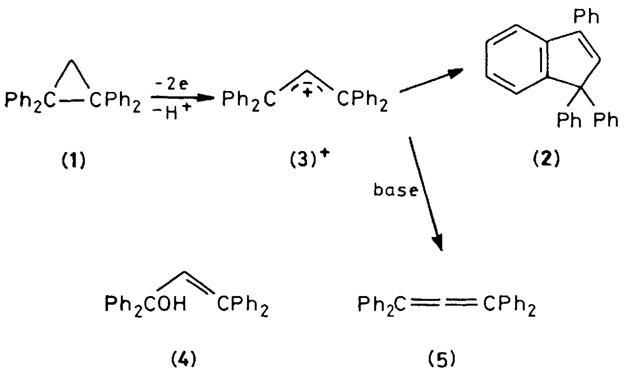
The anodic oxidation of 1,1,2,2-tetraphenylcyclopropane leads to 1,1,3-triphenylindene or tetraphenylallene depending on the basicity of the medium.

We have reported the photosensitized (electron transfer) ring cleavage of 1,2-diphenyl-[1] and 1,1,2,2-tetraphenyl-cyclopropane (**1**)[2]. These reactions presumably involve the 1,3-radical cations; little is known about this class of intermediates. Much of our understanding of the nature of the analogous 1,2-radical cation comes from studies of the anodic oxidation of olefins,[3] therefore, we have applied these techniques (controlled-potential electrolysis, spectroelectrochemistry, and cyclic voltammetry) to the cyclopropane (**1**).

Controlled potential (1.3 V *vs.* Standard Calomel Electrode) electrolysis of (**1**), in acetonitrile with tetraethylammonium perchlorate (0.1 M TEAP) as the supporting electrolyte gives 1,1,3-triphenylindene, (**2**), in good yield (Scheme 1). The anolyte turns purple as soon as the potential is applied. The visible absorption spectrum of this solution shows three maxima (568, 460, and 382 nm) of *ca.* equal intensity. This



Scheme 1

spectrum coincides with that of the 1,1,3,3-tetraphenylallyl mono-cation (**3**)$^+$ which can be generated by treatment of 1,1,3,3-tetraphenylpropen-3-ol, (**4**), with trifluoroacetic acid (TFA).

The proposed cyclization of the cation (**3**)$^+$ is in apparent contradiction of the reported behaviour.[4] Treatment of the allyl alcohol (**4**), with toluene-*p*-sulphonic acid in ethyl acetate gave an almost quantitative yield of tetraphenylallene, (**5**). Using standard alcohol dehydration conditions (10^{-2} M TFA in benzene), analysis of the reaction mixture indicates that (**5**) is the major product [(**5**) 94%; (**2**) 6%]. However, when the solvent for dehydration is acetonitrile with 0.1 M TEAP (10^{-2} M TFA), (**2**) is the major product (97%). Further work has shown that the ratio (**5**):(**2**) is dependent upon the basicity of the conjugate base of the acid used to catalyse the dehydration. Allene formation is favoured by stronger conjugate bases. Thus, the formation of (**5**), at the expense of (**2**), should be favoured when base is added to the anolyte.

When the controlled-potential electrolysis of (**1**) is carried out in acetonitrile (0.1 M TEAP) to which 2,6-lutidine (0.1 M) has been added, the purple colour is not evident and the allene is the major product (50%). The indene is not detected.

Cyclic voltammetric studies on (**1**) reveal two irreversible anodic waves (E_{p1} = 1.36, E_{p2} = 1.58 V). The first wave, attributed to the oxidation of (**1**), is clearly irreversible ($E_p - E_{p2}$ = 130 mV). The appearance of the purple colour, characteristic of the allylic cation (**3**)$^+$ coincides with the onset of the first wave.

As the sweep rate increases from 50 mV s^{-1}, the relative height of the second wave decreases and is not detected at sweep rates greater than 1.0 V s^{-1}. We attribute this wave to the oxidation of (**2**). The sweep rate dependence is simply the result of a relatively slow chemical step leading to this product.

If the voltage is swept anodically to the first oxidation wave and then cathodically, a small reversible reduction wave is observed at $E_{1/2} = +0.34$ V. The intensity of this reversible wave decreases if the cathodic sweep is delayed. We assign this wave to the reduction of the allylic cation (**3**)$^+$ to the radical (**3**)$^\cdot$. When the cation (**3**)$^+$ is generated, in the electrolysis cell, from the alcohol (**4**) by treatment with TFA, the voltammogram of the resuting purple acetonitrile solution has the same reversible reduction wave.

Some uncertainty remains regarding the reaction sequence leading from (**1**)$^{+\cdot}$ to (**3**)$^+$. There is no evidence for two one electron transfer steps in methylene chloride, which stabilize radical cations,[5] even at sweep rates as high as 20 V s^{-1}. We have prepared an extensive series of *p*-substituted 1,1,2,2-tetraphenylcyclopropanes;[6] we may be able to observe the 1,3-radical cation in some cases. In fact, two closely spaced (190 mV), equally intense waves are observed upon oxidation of the 1,1,2,2-tetrakis(4-cyanophenyl)cyclopropane. These results will be reported in the full account of this work.

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