Selective Allylic Electron-transfer Oxidation of β-Ionone

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The reactions of β-ionone with one-electron oxidizing agents, in methylene chloride/alcohol, afford allylic oxygenated derivatives; the reactions are likely to proceed *via* a one-electron transfer mechanism.

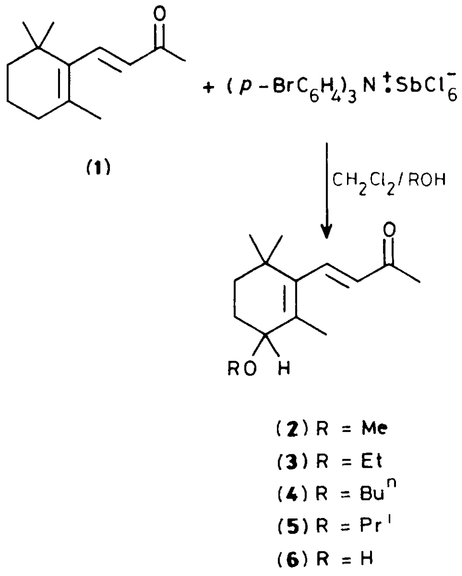
Numerous papers have been devoted to the thermal generation of cation radicals, by reaction of unsaturated substrates with several one-electron oxidizing agents.[1] Cation radicals, by virtue of their dual functionality, undergo reactions with nucleophiles,[2] superoxide anion,[3] or molecular oxygen,[4] form dimeric products,[5] or disproportionate into charged ions.[6]

Proceeding in our research on the thermal generation of cation radicals, and on their chemical evolution,[7] we report that the reactions of β-ionone (**1**) with tris-*p*-bromophenylammoniumylhexachloroantimonate ($(p\text{-BrC}_6\text{H}_4)_3\text{N}^{\cdot+}$ SbCl_6^-, in methylene chloride/alcohol, led to allylic oxygenated derivatives (**2**)—(**6**), important end-group synthons in the synthesis of carotenoids.[8]

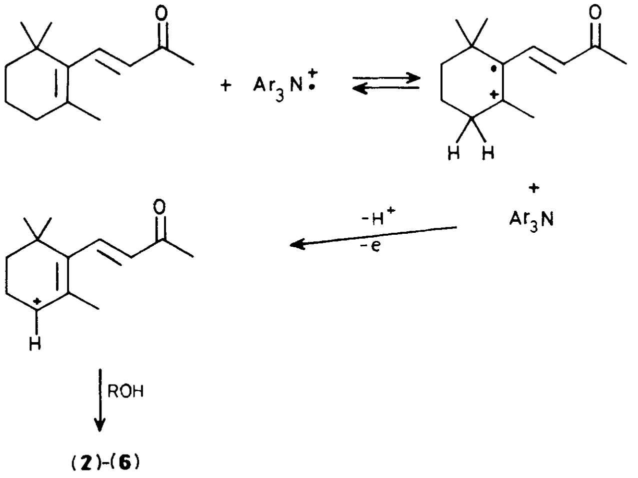
Typical conditions are as follows: (**1**) (0.1 mmol) was dissolved in methylene chloride/alcohol (20 ml; 9/1 v/v) at room temperature and air atmosphere, and an equimolar amount of the aminium salt (0.1 mmol) was added to the stirred solution. The reactions were monitored by g.c. and t.l.c. until the starting material had totally disappeared (overnight). The products, isolated by column chromatography on silica gel (light petroleum/ethyl ether, 9 : 1, as eluant), were fully characterized by ^{1}H, ^{13}C, APT ^{13}C n.m.r., g.c.–mass spectrometry, and i.r. spectroscopy, and by comparison with authentic samples synthesized by methods reported in the literature.†‡

The previous methods used for the introduction of oxygenated substituents into the allylic positions of (**1**),[9]‡ are of interest for mechanistic implications, and include the recent direct and/or indirect anodic electro-oxidation of (**1**) reported by Utley and co-workers;[10] and affording, in acidic solution, in the presence of sodium acetate, 3-acetoxy-β-ionone and/or 3-hydroxy-β-ionone (**6**). The success of this procedure was strictly related to the oxidation potential of (**1**). In fact, cyclic voltammetric experiments on (**1**), at a platinum microelectrode (MeCN–$\text{Bu}_4\text{N}^+\text{ClO}_4^-$, 0.1 M), showed two irreversible peaks at 1.34 and 2.00 V *vs.* Ag/Ag$^+$. These values, particularly the oxidation potential of the first wave, suggested to us that the substrate (**1**) could behave as an electron rich-alkene (vinyl ether), undergoing an easy functionalization *via* electron-transfer process, thermally and/or photochemically induced.[4,11]

On the basis of the particular features of our one-electron oxidizing agent, showing an exceedingly low reduction potential [E^{red} = 1.15 V *vs.* standard calomel electrode (S.C.E.)][12] the observed results could be plausibly accommodated as reported in Scheme 2.[10] Although the first step is fairly endoergonic,[13] the subsequent reactions, *i.e.*, the proton loss from the primary cation radical ($\mathbf{1}^{\cdot+}$) and the subsequent oxidation step could drive the overall process. Alternatively, the second step could only require loss of the hydrogen atom, followed by pairing of the diradical after reorganization. Similar results were also obtained by treatment of (**1**), under the same conditions, *via* a slower reaction, with two equivalents of trityl hexachloroantimonate ($\text{Ph}_3\text{C}^+\text{SbCl}_6^-$), another well known one-electron oxidizing reagent.[14] As expected, the isomer α-ionone, showing on cyclic voltam-



Scheme 1



Scheme 2

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† Compound (**2**): *m/z* 222 (41%), 207(8), 179(8), 151(33), 123(73), 109(15), 91(27), 43(100); i.r. (KBr) ν 2962, 2933, 2859, 1696, 1678, 1613, 1462, 1359, 1253, 1100, 1087, 799, 725 cm^{-1}; ^{1}H n.m.r. (CDCl$_3$) δ 7.24 (d, 1H, *J* 16.5 Hz), 6.18 (d, 1H, *J* 16.5 Hz), 3.56 (t, 1H), 3.41 (s, 3H), 2.32 (s, 3H), 1.81 (s, 3H), 1.80—1.10 (m, 4H), 1.05 (s, 3H), 1.01 (s, 3H); ^{13}C n.m.r. (CDCl$_3$) δ 198.23(1), 142.62(2), 139.77(1), 132.99(2), 132.73(1), 78.56(2), 56.83(4), 34.57(3), 34.49(3), 28.76(4), 27.25(4), 22.78(1), 18.68(4). Consistent spectral data were also obtained for the substrates (**3**)—(**6**).

‡ The products (**2**), (**3**), (**6**) have been prepared following the procedure described in ref. 9 and show identical physical and spectroscopic data to those synthesized by us.

metry an oxidation potential >2 V *vs.* Ag/Ag$^+$, was recovered unchanged in similar reactions with the aminium salt in methylene chloride/alcohol.

The easy procedure, and the high yields of the isolated products (65—75%) are evidence of the potential of this method as a valuable synthetic tool for the preparation of several allylic functionalized derivatives. Also, the physical properties of (**1**) could make possible its functionalization, not only *via* a thermal electron-transfer process, but also *via* sensitized photochemical processes. Thus further work in the area is warranted.

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