Reaction of Protonated t-Butoxyl Radicals with Alkynes; Electron Spin Resonance Spectra of Alkoxyalkene and 1,2-Dialkoxyalkene Radical Cations

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When di-t-butyl peroxide is photolysed in the presence of an alkyne (RC≡CR) under acidic conditions, the resulting protonated t-butoxyl radical adds to the triple bond, and the e.s.r. spectra of the corresponding alkoxyalkene or *vic*-dialkoxyalkene radical cations ($Bu^tOCR{=}CHR^{\cdot +}$ or $Bu^tOCR{=}CROBu^{t\cdot +}$) can be observed.

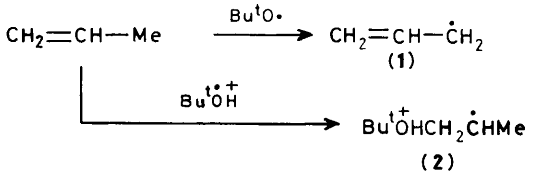
The properties of alkoxyl radicals are transformed by protonation.[1,2] For example t-butoxyl radicals abstract hydrogen from propene to give allyl radicals (**1**), but protonated t-butoxyl radicals add to the double bond to give the distonic radical cations (**2**).[1] We report here an e.s.r. study of the reaction of protonated t-butoxyl radicals with alkynes, which has led to the first observation of the spectra of alkoxyalkene and 1,2-dialkoxyalkene radical cations.

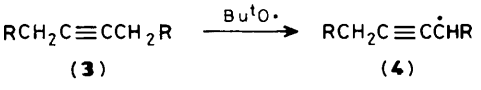
On photolysis of a 1:1 mixture of di-t-butyl peroxide and but-2-yne, hex-3-yne, or oct-3-yne (**3**) in an e.s.r. cavity at *ca.* 200 K, the spectra of the familiar prop-2-ynyl radicals (**4**) (g 2.0027—2.0028)[3] were observed. In contrast, photolysis of a 2:1 mixture of the peroxide and the alkyne in cyclopropane containing trifluoroacetic acid at *ca.* 180 K gave rise to spectra showing hyperfine coupling to two non-equivalent alkyl groups, RCH_2, and to one further proton, and with a high g value (2.0033—2.0036), suggesting delocalisation of the unpaired electron onto oxygen. Experiments with CF_3CO_2D showed that the unique proton was derived from the acid. We assign these spectra to the alkoxyalkene radical cations (**5**), which are isoelectronic with allyl radicals. One of the alkyl groups lies close to the nodal plane of the SOMO, and shows only a small hyperfine coupling. Typical values of the hyperfine coupling constants are, for (**5**; R = H), a(3H) 23.91, a(1H) 16.44, a(3H) 4.98 G; and for (**5**; R = Me), a(2H) 28.68, a(1H) 16.71, a(2H) 8.98 G, at 180 K.

Support for the assignment of the spectra to the radical cations (**5**) was obtained by γ-radiolysis of alkoxyalkenes in a $CFCl_3$ matrix; this is established as a specific method for preparing radical cations. Under these conditions, the product from $Bu^tOCH{=}CH_2$ showed a spectrum with a(2H) 18.44 G, g 2.0034, ΔH_{pp} 9 G at 146 K, and that from $Bu^tOCH{=}CHMe$, a(3H) 25.8, a(1H) 13.0, a(1H) 4.5 G, g 2.0031, ΔH_{pp} 3 G at 127 K (ΔH_{pp} is the peak-to peak distance). These g values, and the spin distributions indicated by the hyperfine coupling constants, are similar to those which we observe for the radical cations (**5**). However, we are not able to determine whether the radical cations (**5**) have the *Z*-configuration, or the *E*-configuration as has arbitrarily been assumed.

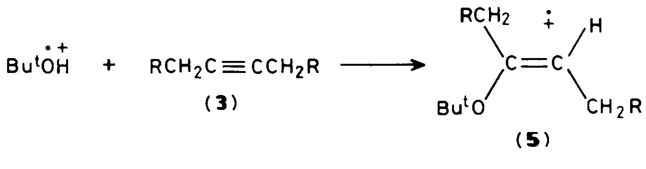
When the concentration of di-t-butyl peroxide in the reaction mixture was increased, the product from but-2-yne (**3**; R = H) showed two superimposed spectra consisting of simple septets, ΔH_{pp} 0.35, a(6H) 10.98 G, g 2.0040, and a(6H) 9.69 G, g 2.0041, at 219 K in the concentration ratio 1:1.9. We assign these spectra to the *E*- and *Z*-forms of the 2,3-di-t-butoxy-but-2-ene radical cations (**6**) and (**7**).

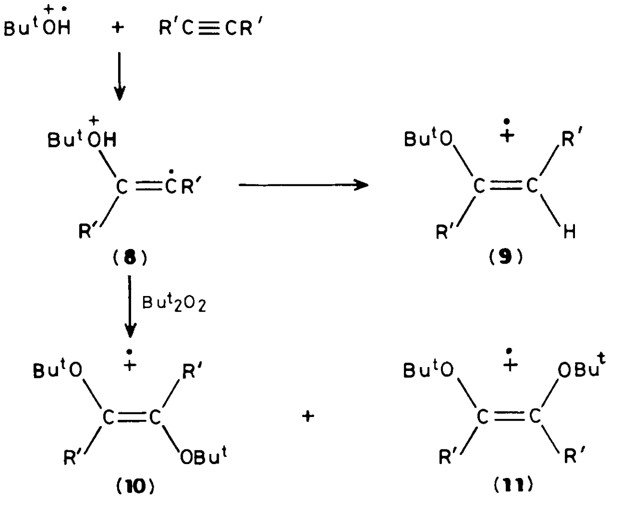
This assignment is supported by the observation that (*E*/*Z*)-1,2-di-t-butoxyethene reacts with $(4\text{-}BrC_6H_4)_3N^{\cdot +}$ $SbCl_6^-$ in dichloromethane at 198 K to give a product showing a triplet spectrum, a(2H) 8.25 G, g 2.0049, ΔH_{pp} 1.125 G. Similar spectra were obtained when the alkene in dichloromethane was treated with trifluoroacetic acid (or CF_3CO_2D) at 246 K, or when a solid solution in $CFCl_3$ was γ-irradiated at





R = H, Me or Et





77 K then annealed to 158 K, and we assign these spectra to the corresponding radical cation (E/Z)-$\mathrm{Bu^tOCH{=}CHOBu^{t\cdot+}}$.

The formation of the alkoxyalkene radical cations can be rationalised as follows. Protonation of the t-butoxyl radical increases its electrophilic character, and it adds to the triple bond of the alkyne, as it does to the double bond of an alkene, to give the distonic vinyl radical cation (**8**). Vinyl radicals however are normally too reactive for their spectra to be observed under the conditions of photolytic generation. When the concentration of the peroxide is low, the monoalkoxyalkene radical cation (**9**) is formed by rearrangement (or by abstraction of hydrogen from CF_3CO_2H), but when the peroxide concentration is high, bimolecular reaction occurs between the radical (**8**) and the peroxide to generate the E- and Z-dialkoxyalkenes, which are then oxidised by $\mathrm{Bu^tOH^{\cdot+}}$ to the corresponding radical cations (**10**) and (**11**).

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